EXHIBIT 1

IN THE UNITED STATES DISTRICT COURT FOR THE NORTHERN DISTRICT OF WEST VIRGINIA AT CLARKSBURG

| | — X |
|--|--------------------------------------|
| ACTELION PHARMACEUTICALS LTD, Plaintiff, | : : Civil Action No. 1:20-CV-110-JPE |
| v. | · : |
| MYLAN PHARMACEUTICALS INC., | : : |
| Defendant. | : : |
| | : : x |

DECLARATION OF WILLIAM T. HENSLER, PH.D. IN SUPPORT OF MYLAN'S CLAIM CONSTRUCTION BRIEFING

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- I, William T. Hensler, Ph.D., pursuant to 28 U.S.C. § 1746, declare as follows:
- 1. I submit this Declaration in support of Mylan Pharmaceuticals Inc. ("Mylan" or "Defendant")'s Claim Construction Brief to offer my opinion on the meaning of certain claim terms of U.S. Patent Nos. 8,318,802 ("the '802 patent") and 8,598,227 ("the '227 patent") (collectively, "the patents" or "the patents-in-suit") as a person of ordinary skill in the art (a "POSA").
- 2. I may also testify or otherwise offer rebuttal opinions to any opinions offered by expert(s) testifying on behalf of Actelion Pharmaceuticals Ltd ("Actelion" or "Plaintiff").

I. QUALIFICATIONS

- 3. I previously submitted an expert report in this matter on October 22, 2021 ("Rebuttal Report") where I outlined my qualifications and experience. I have briefly summarized those here.
- 4. I graduated with a B.S. in chemical engineering with honors from Rutgers University-New Brunswick in 1980. Subsequently, I obtained an M.S. in biomolecular engineering from Cornell University with honors in 1982. I later earned my Ph.D. in biochemical engineering and biotechnology from Rutgers University-New Brunswick in 1994.
- 5. I am currently a principal consultant for Alantra Biopharma Services, LLC. As a principal consultant, I provide pharmaceutical consulting services in the life sciences sector, including strategic and organizational planning, due diligence on IP, process development and qualification, and cGMP support and engineering design of facilities (up to BSL-3) for biologics, vaccines and therapeutic proteins. This includes design, procurement, startup, qualification, calibration and operation of equipment and instrumentation in accordance with cGMP, for the pharmaceutical industry. I have expertise across the unit operations and test methods used to produce bulk drug substances and drug product, including the formulation and preparation of

media and buffers for cell culture operations, all of which involve the sampling, measurement and adjustment of pH.

- 6. From 1999 to 2012, as Principal of Alantra BioPharma Services, LLC, I performed a variety of services for the pharmaceutical and biotechnology industry, including assignments such as pharmaceutical facility design, start-up and qualification (IQ/OQ/PQs), and development of user requirement specifications (URSs). I procured and oversaw the installation of equipment and instrumentation for these industries, including in-line and bench top instruments. I also performed instrument and equipment acceptance testing at vendor's factories (FATs) and pharmaceutical companies (SATs). Additionally, I established and implemented cGMP instrument calibration programs that included both in-line and benchtop pH instrumentation. Further, I developed instrument cleaning and use logs, preventive maintenance programs, performed troubleshooting of facilities and instruments, determined root cause analysis for out of spec products, and developed corrective and preventative actions (CAPAs). I also performed process qualification for numerous biologicals and vaccines according to ICH Guidelines Q7 and Q8(R2), some of which are now FDA-approved. In this role, I performed process validation of monoclonal antibody and fusion proteins for biologics in development, wrote validation master plans, validation protocols, and executed IQ/OQ/PQ equipment protocols.
- 7. However, my qualifications and credentials are set forth more fully in my *curriculum vitae*, attached as Exhibit A.

II. COMPENSATION AND PRIOR TESTIMONY

- 8. I am being compensated for my time at the rate of \$590 per hour. My compensation is not dependent on the substance of my opinions or testimony, or the outcome of this case.
- 9. Most recently I have testified at a claim construction hearing offering expert testimony in a patent infringement case involving the use of bioreactors for autologous gene

therapy (CAR-T cell therapy). Prior to that, I was deposed in this matter regarding my Rebuttal Report and opinions therein.

III. MATERIALS REVIEWED

10. In arriving at my opinions in this Declaration, I have considered my training, knowledge, basic texts and scientific principles, experience in the relevant scientific disciplines, and the materials cited herein.

IV. LEGAL STANDARDS

A. Claim Construction

11. I understand from counsel that the claims of a patent define the invention to which the patentee is entitled the right to exclude. I have been informed by counsel that generally claim terms are given their "ordinary and customary" meaning. I have been informed that this has also been referred to as the "plain and ordinary" meaning and I use these descriptions synonymously throughout this report. In other words, claim terms are generally defined by the meaning the term would have had to a POSA¹ as of the effective filing date² of the patent application. I have also been informed by counsel that unless some other reason exists, *i.e.*, a claim construction order, a

¹ I previously opined in this matter that a POSA for the patents-in-suit would have had skills in pharmaceutical sciences with an understanding in formulation and development of pharmaceuticals. A POSA would have had a Ph.D. in pharmacy, chemistry, or a related field, with at least two years of post-graduate laboratory/industrial experience in, for example, the research and development of formulations for the preparation of drug substances. A POSA's experience would include, among other things, formulating injectable and/or lyophilized drug products, developing processes for making injectable and/or lyophilized drug products, and measuring pH. Such a person would have understood that the process requires a multidisciplinary approach, and would have drawn upon not only his or her own skills, but also could have taken advantage of certain specialized skills of others to solve any given problem. I use the term "POSA" here to mean "skilled artisan," which I understand to signify the same concept.

² I understand from counsel that the effective filing date, the alleged "priority date," for the patents-in-suit is February 3, 2006.

claim term should be accorded its plain and ordinary meaning as understood by a POSA (at the relevant priority date) when read in the context of the specification and prosecution history.

12. I understand that the Federal Circuit has issued an opinion vacating the district court's previous construction of the term "pH of 13 or higher" to mean "pH of 12.5 to 13.4, or higher." I further understand that the Federal Circuit's opinion directed the District Court on remand to construe the term "pH of 13 or higher" in light of extrinsic evidence,³ including three textbooks that Plaintiff previously introduced: Hans van Kessel et al., CHEMISTRY 12, Chapter 8.1 (2003) ("Kessel"), Frank Mustoe et al., CHEMISTRY 11, Chapter 10 (2001) ("Mustoe"), and Martin S. Silberberg, CHEMISTRY: THE MOLECULAR NATURE OF MATTER AND CHANGE, Chapter 18 (4th ed. 2006) ("Silberberg")⁴. In addition, I understand that the Federal Circuit directed the District Court to consider this evidence with a focus on "whether a pH of 13 carries any meaning to a person of ordinary skill in the art as regards precision of measurement, significant digits, or rounding."

V. SUMMARY OF OPINIONS

- 13. I provide the testimony below from the perspective of a POSA as defined above as of the effective filing date of the patents.
- 14. A POSA would understand that the "plain and ordinary meaning" of "a pH of 13 or higher" implies a pH of 13.0 or higher if measured under standard manufacturing conditions, or

³ I understand from counsel that "extrinsic evidence" is evidence external to the patents and associated file histories (which I understand are referred to as "intrinsic evidence"), and includes evidence such as expert testimony, dictionaries, and technical treatises and articles.

⁴ Kessel is attached hereto as "Exhibit B" and, as I understand, was previously submitted by Plaintiff as ECF No. 63, Exh. 6. Likewise, Mustoe is attached hereto as "Exhibit C" and was previously submitted as ECF No. 63, Exh. 7 and Silberberg is attached hereto as "Exhibit D" and was previously submitted as ECF No. 63, Exh. 10.

13.00 or higher under more precise analytical testing. Specifically, a POSA would understand that a whole-number pH value given in the context of these patents and the field of pharmaceutical development necessarily implies a decimal point and at least one significant figure of "0" (zero) to the right of the whole number.

- 15. A POSA would reference industry standards in existence at the time of the patents, such as those of the United States Pharmacopeia ("USP") and/or the National Institute of Standards and Technology (NIST), to determine the margin of error of a reported pH value of "13."
- 16. To the extent any variation from "13" is allowed, a POSA using conventional pH meters and applying their conventional understanding of the measurement errors associated with pH meters at the time of the priority date would understand that a claim term referring to a "pH of 13" would mean at most a pH of 12.98 or higher.
- 17. In no case would a pH value of "13 or higher" include a value of pH 12.5, nor would it allow for rounding down based on the order of magnitude of the pH. This would introduce such unacceptably large error well outside the pH tolerances a POSA accepts and is accustomed to in developing and manufacturing pharmaceuticals.
- 18. Further, reading "pH of 13" to allow a pH of 12.5 is well outside the standard and expected degree of pH measurement accuracy using available instrumentation and methods at the time, and is inconsistent with standards (USP, NIST) in effect as of the effective filing date.

VI. BRIEF TECHNICAL BACKGROUND

19. A POSA has chemical training and understands the claims of the patents as a chemist, regardless of whether my POSA definition or Plaintiff's POSA definition is used. A POSA is not merely a mathematician; a POSA understands the techniques and instruments that applied chemists use to make pH measurements, namely pH meters.

- 20. That is not to say a POSA versed in chemistry would not be familiar with abstract rules of rounding or "significant figures," but a POSA with chemical training would also understand that as of the priority date and well before, pH meters could measure to two decimal places (precision) with a level of accuracy⁵ of at least 0.02 pH units. USP 791 (2005), USP 791 (1995), USP 791 (1985). Furthermore, as discussed below, national standards prescribed a standard margin of error of at most 0.02 pH units on either side of a pH value.
- 21. My opinion is informed by basic principles of what "pH" measures and the information a POSA understands a pH value to convey.

A. Measuring pH and the pH Scale

22. The scientific term "pH" is a common term used in the art for at least a hundred years before the priority date. The "p" stands for "power" and the "H" stands for the concentration of hydrogen ions, which are measured in mol/L (also known as molarity). Underlying the term is the negative of the logarithm to the base ten of the hydrogen ion concentration. This essentially takes a very small number and converts it into one that is easier to express. As Kessel explains:

$$pH = -log[H_{(aq)}^+]$$

Ex. B, Kessel 540.

23. The hydrogen ion concentration of a solution ("H+" or "H₃O+") inversely correlates to the measured and recorded pH value of a given solution using the simple relationship in the above equation. The higher the concentration of hydrogen ions, the lower the pH. In other words,

⁵ I use "accuracy" and "measurement error" and/or "error" as interchangeable throughout this Declaration with the understanding that "error" is an aggregate of factors which include instrument accuracy, precision, linearity, calibration and sample handling.

as the concentration of hydrogen ions increases in a given solution, it becomes more acidic and the pH decreases.

24. An acidic solution has a pH of less than 7.00. When the hydrogen and hydroxide ions are equal, the solution is said to be neutral—*i.e.*, it has a pH of 7.00. When the hydroxide ions exceed the amount of hydrogen ions, the solution is said to be basic, *i.e.*, a pH greater than 7.00. This is shown in the following table in Mustoe.

| acidic solution | greater than 1×10^{-7} | $[H_3O^+] > [OH^-]$ | < 7.00 |
|------------------|---------------------------------|---------------------|--------|
| neutral solution | 1×10^{-7} | $[H_3O^+] = [OH^-]$ | 7.00 |
| basic solution | less than 1×10^{-7} | $[H_3O^+] < [OH^-]$ | > 7.00 |

Ex. C, Mustoe 388.

- 25. The pH scale is used to express the concentration of hydrogen ions in positive numbers, rather than negative exponents. For example, the pH of neutral solution at SATP⁶ is 7.00, which is the same thing as " 1.0×10^{-7} ." Ex. B, Kessel at 541.
- 26. In the expression "1.0 x 10⁻⁷," the term "10⁻⁷" is not a hydrogen ion concentration. It is a power of ten that only indicates where to place the decimal point. For example, for 1.0 x 10⁻⁷ the concentration of hydrogen ions per mol/L would be 0.0000001. *See e.g.*, Ex. B, Kessel at 540-41. The table below from Mustoe shows this relationship. For every whole number pH, the exponential notation corresponds to the hydrogen ions [H₃O⁺] (mol/L) and the negative log:

⁶ "SATP" means standard atmosphere, temperature, and pressure.

| Range of acidity and basicity | [H ₃ 0+] (mol/L) | Exponential notation (mol/L) | log | pH (-log [H ₃ 0+]) | |
|---|-----------------------------|------------------------------|-----|----------------------------------|--|
| strong acid | 1 | 1×10^{0} | 0 | 0 | |
| | 0.1 | 1×10^{-1} | -1 | 1 | |
| | 0.01 | 1×10^{-2} | -2 | 2 | |
| | 0.001 | 1×10^{-3} | -3 | 3 | |
| | 0.000 1 | 1×10^{-4} | -4 | 4 | |
| | 0.000 01 | 1×10^{-5} | -5 | 5 | |
| | 0.000 001 | 1×10^{-6} | -6 | 6 | |
| neutral $[H^+] = [OH^-]$ $= 1.0 \times 10^{-7}$ | 0.000 000 1 | 1 × 10 ⁻⁷ | -7 | 7 | |
| | 0.000 000 01 | 1×10^{-8} | -8 | 8 | |
| | 0.000 000 001 | 1×10^{-9} | -9 | 9 | |
| | 0.000 000 000 1 | 1×10^{-10} | -10 | 10 | |
| | 0.000 000 000 01 | 1×10^{-11} | -11 | 11 | |
| | 0.000 000 000 001 | 1×10^{-12} | -12 | 12 | |
| | 0.000 000 000 000 1 | 1×10^{-13} | -13 | 13 | |
| strong base | 0.000 000 000 000 01 | 1×10^{-14} | -14 | 14 | |

Ex. C, Mustoe at 387. The way to calculate pH is shown below:

∴ pH =
$$-\log [H_3O^+]$$

= $-\log (1.0 \times 10^{-7})$
= $-(-7.00)$
= 7.00

Id.

When determining the pH value of a given solution, the POSA understands that the digits following the decimal point are equal to the number of significant digits in the hydrogen ion concentration. Ex. B, Kessel at 541. That is because pH is a logarithmic scale that *measures the concentration of hydrogen ions in a solution*. In other words, the value does not reflect an abstract

power of ten or number of zeros. A POSA understands it refers to an underlying value that is directly measurable. It does not refer to an abstract mathematical formulation.

- 28. A POSA understands that in any pH value expressed as a whole number, there is always, and necessarily, at least one implied significant figure following the decimal point. This is illustrated in the table from Mustoe. Consider "1.0 x 10⁻⁷." The "1.0" in front of the 10⁻⁷ means there are two significant figures, the "1" and the "0." Ex. C, Mustoe at 387, Table 10.7. Those two significant figures are illustrated in the pH value of "7.<u>00</u>" as the two digits to the right of the decimal point as shown above. *Id.* at 387.
- 29. The digits to the left of the decimal are *not* significant in a pH value. As mentioned above, that is because that digit is derived from the power of ten and is only indicative of where the decimal point lands. *See e.g.*, Ex. C, Mustoe at 387.
- 30. For example, a hydrogen ion concentration of 3.7×10^{-3} has two significant figures. The "3" and "7" are both considered significant; the " 10^{-3} " is not. Translating that to the pH value for that hydrogen ion concentration, you arrive at the below:

$$pH = -log [H3O+]$$

= $-\log (3.7 \times 10^{-3})$ (two significant figures)

= 2.43 (two digits following the decimal point)

Therefore, the solution has a pH of 2.43.

31. With respect to the claims here, the patents-in-suit claim a pH value—they do not claim the number "13" in the abstract. As outlined above, a POSA would understand that for every whole-number pH value (i.e., a pH value expressed as an integer) there is *at least one* significant figure and it can *only* be to the right of the decimal place. Again, the digits to the left of the decimal place are *not* significant. They only show the power of 10 by which the underlying concentration

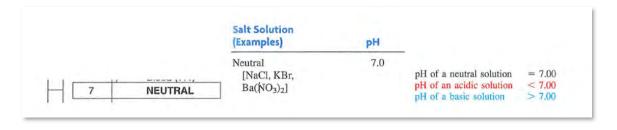
is multiplied. *See* Ex. E, Harvey⁷ 14 ("For measurements using logarithms, such as pH, the number of significant figures is equal to the number of digits to the right of the decimal, including all zeros. Digits to the left of the decimal are not included as significant figures since they only indicate the power of 10. A pH of 2.45, therefore, contains two significant figures.").

32. In other words, even if the digits following the decimal point are removed when written (*i.e.*, 7.00 to 7) a POSA understands that the pH value must include at least one significant figure ("0" or "00," depending upon the expected degree of precision) after the decimal place. A POSA would understand that there is *always* an implied significant figure in a pH measurement due to the logarithmic nature. That is because there is always a multiplier in front of the power of 10 (*i.e.*, 1.0 or 1). Table 10.7 of Mustoe shows this for a pH of 13:

| 0.000 000 000 000 1 | 1×10^{-13} | -13 | 13 |
|---------------------|---------------------|-----|----|
| | | | |

Mustoe at 387. Because there must always be at least the "1" multiplier in order for the pH value to reflect an underlying hydrogen concentration, 1×10^{-13} is necessarily equivalent to a pH of 13.0.

33. As all of these textbooks show, the fact that a whole-number pH value necessarily implies one significant digit of zero means it is customary to drop the zeros following the decimal point when reporting pH values. In Silberberg, for example, a "neutral" pH is defined in all three ways:



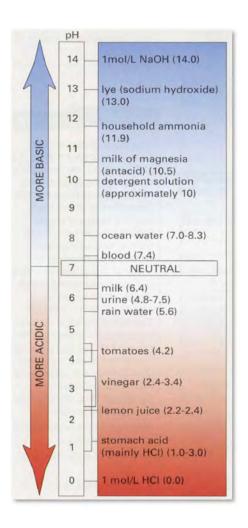
⁷ David Harvey, Modern Analytical Chemistry, Chapter 2 (2000) ("Harvey").

Ex. D, Silberberg 775, 797. Kessel equates the terms "pH 3.0," "1 x 10⁻³," and "pH 3":

Note that the hydrogen ion concentration changes by a multiple of 10 for every increase or decrease of one pH unit. For example, at pH 4.0, $[H^+_{(aq)}]$ is 1×10^{-4} mol/L; at pH 3.0, $[H^+_{(aq)}]$ is 1×10^{-3} mol/L. At pH 3, the $H^+_{(aq)}$ concentration is ten times higher.

Ex. B, Kessel 541.

- 34. pH values are said to fall along the "pH scale," which in shorthand is often expressed as ranging from "0" to "14." Also in shorthand, "neutral" pH is often expressed as "7." As I have explained, however, a POSA understands whole numbers like "pH of 7" to refer to "pH of 7.0" or "pH of 7.00." Ex. B, Kessel at 541 ("In pure water, and in any neutral solution at SATP, the concentrations of hydrogen and hydroxide ions are equal, and therefore the pH is 7.00.").
 - 35. An illustration of the pH scale is below:



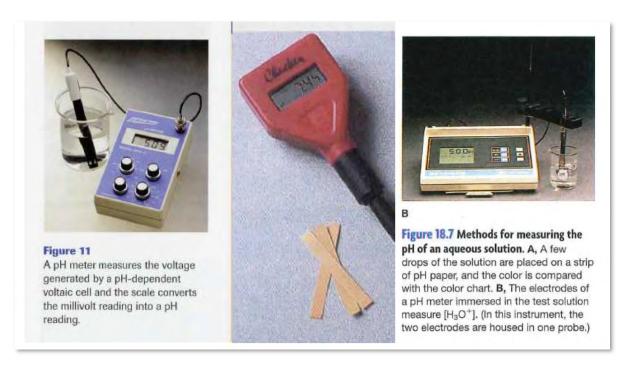
Ex. C, Mustoe at 388.

36. I understand that Plaintiff may take the position that the claim term a "pH of 13" should refer to an "order of magnitude." For the reasons described above, no POSA would read the term that way, because a power of ten is not a pH value.

B. pH Meters, Precision, and Accuracy

- 37. In order to measure a solution's pH as of the priority date, a POSA in the field of pharmaceutical sciences would use a pH meter.
- 38. pH meters are electronic instruments that measure the "voltage generated by a pH-dependent voltaic cell and the scale converts the millivolt reading into a pH reading." Ex. B, Kessel

- at 544. The pH meter was an improvement on a much cruder form of measurement, litmus paper or pH paper, which these days is typically used as a teaching tool.
- 39. An important distinction between pH meters and litmus paper is that a pH meter is capable of measuring with precision down to two or three significant figures (*i.e.*, two or three decimal places). Using litmus paper results in a color change to quickly "estimate" the pH of a solution. *See* Ex. D, Silberberg at 777. Generalized estimates are not useful information for a POSA in the pharmaceutical sciences. pH meters would be used.
- 40. I will discuss the accuracy, or error measurement, of pH meters further below. At the outset, it is important to note the concept of sensitivity (or resolution), *i.e.*, the number of decimal places that standard pH meters could display as of the priority date, which is related to the expected margin of error.
- 41. Plaintiff's chemistry textbooks have three examples of pH meters. All three show that, consistent with a POSA's expectations, they measure pH down to two decimal places (two significant figures).



- Ex. B, Kessel 544; Ex. C, Mustoe 391; Ex. D, Silberberg 777, respectively.
- 42. pH meters at the priority date of the patents-in-suit were highly sensitive, and as illustrated above, were able to measure to at least two decimal places. Indeed, there were pH meters with even greater resolution, with a precision to three decimal places. *See infra* ¶¶ 49-55 (discussion on USP and Harris at Table 15-3).
- 43. A POSA in the pharmaceutical sciences would not only rely upon basic chemistry textbooks from early on in his or her chemistry education. Rather for applied chemistry, they would look primarily to industry and governmental standards.
- 44. One source a POSA would consult is the United States Pharmacopoeia, or "USP." USP is a compendium of (pharmacopoeia) tests providing standards and protocols for many pharmaceutical raw materials and finished products.
- 45. Testing and compliance to these standards and protocols is a basic requirement for global manufacturing, release and distribution of pharmaceutical ingredients and drug products. In cases where USP test methods exist (including pH testing), developers and manufacturers of human drugs are explicitly referred to them by guidelines endorsed by the Food and Drug Administration (FDA).
- 46. Like the textbooks Plaintiff introduced, USP 791 (2005 edition) and USP 791 (2006 edition)⁸ showed that pH meters were sensitive to two decimal places, including reporting a pH of 13.00 (Calcium Hydroxide, Saturated at 25°C).

⁸ Attached hereto as Exhibits F and G, respectively.

| Tempera- | Potassium Tetraoxalate, | Potassium Biphthalate, 0.05 m | Equimolal Phosphate, 0.05 m | Sodium Tetraborate, 0.01 m | Calcium Hydroxid Saturated at 25° |
|------------------|----------------------------------|----------------------------------|--------------------------------|--------------------------------|--------------------------------------|
| ture, °C | 0.05 m | 4.00 | 6.92 | 9.33 | 13.00 |
| the come | louteon of 1.67 | de louno 4.00 outrolles | 6.90 | 9.28 | of sand 12.81 and |
| 13 | 1.68 | 4.00 of should | 6.88 | nds, for west tor P | 08 317018 112.63 |
| 20 | | nd or slop dol. Mes | 6.86 | ual monogane. The test o | brytom ad12.45 |
| 25 | 1.68 1.68 | | 6.85 | 9.14 bupt | To bilos 912.29' 891 |
| 30 | | The pH sc 20.4 defined by | 6.84 | more 19.10 momu | man 12.13 a |
| 35 | 1.69 | 4.04 | 6.84 | nd Calcu70.0 ns Proceed | Te89.11 cedane, an |
| 40 | 1.69 | 4.05 | 6.83 | e Court 40.9 under Part | Ob. 48.11 ion Particl |
| 45 | 1.70 | which E ar 4.06 are the me | 6.83 | 9.01 | 11.71 mon |
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| dt 555 H | g ve being 1.72 T. Ison is | 4.08 | OMMONIO INSPECT | sport of 8.96 to radius | test 11.45 average mi |
| 60 | 1.72 | 4.09 | n the uni 48.6 ed | imber of 106.8 ies present i | not exceed the approx |
| THE TOTAL TRAILS | CHOCK THE SHIRTSHIP SHIP KEEN IV | mine and fratmanders for | SCRISVE SHI H. L | SIGNA MILL DISTORD THE A MELLE | Laufelle and passages and |

See, e.g., Ex. F, USP 791 (2005), MYLAN_EPO_000109 at 111.

47. This is consistent with a POSA's understanding of significant figures in the reported pH value for a given concentration of hydrogen ions. For all of these pH values, the significant figures are only those to the right of the decimal place.

C. Measurement Error

- 48. Inherent in most measurements is an allowable "measurement error," or the variance of a measurement that is considered sufficiently accurate. In the field of pharmaceutical sciences, precise and accurate measurements are paramount and the range of permissible error is correspondingly narrow.
- 49. As explained in the USP 791 (2005)⁹: "For compendium purposes, pH is defined as the value given by a suitable, properly standardized, potentiometric instrument (pH meter) capable **of reproducing pH values to 0.02 pH unit**." Ex. F, USP 791 (2005), MYLAN_EPO_000109 at 110; *id* at 111 ("Repeat the standardization until both Buffer Solutions for Standardization give observed pH values within 0.02 pH unit of the tabulated value without further adjustment of the controls."). Notably, the USP was making similar statements 20 years before the priority date of the patents. *See* Ex. H, USP 791 (1995), Ex. I, USP 791 (1985).

⁹ According to the cover of USP 2005, it became official as of January 2005.

- 50. Standards endorsed by the United States National Institutes of Standards and Technology (NIST) have also spoken to expected measurement error for pH meters. The NIST is a federal agency tasked with developing and promulgating standards for calibration and measurement.
- 51. This is shown in another textbook that existed as of the priority date, Daniel C. Harris, QUANTITATIVE CHEMICAL ANALYSIS, Chapter 15 (3d ed. 1991) (Harris). Under the heading "Errors in pH Measurement," Harris explains:

Our knowledge of an analyte's pH cannot be any better than our knowledge of the pH of the buffers used to calibrate the meter and the electrode. This error is typically on the order of ± 0.01 pH units.

52. Harris explains that this margin of error is endorsed by the NIST:

Many pH standards are available commercially. The pH of the solutions in Table 15-3 were measured at the U.S. National Institute of Standards and Technology and are considered to be accurate to ± 0.01 pH units.

Ex. J, Harris 129.

53. Table 15-3 of Harris is reproduced below which shows pH measurements to the thousandth place (three decimal places):

| Temperature (°C) | Saturated (25°C) potassium hydrogen tartrate | 0.05 m potassium dihydrogen cîtrate | 0.05 m potassium hydrogen phthalate | 0.025 m potassium dihydrogen phosphate 0.025 m disodium hydrogen phosphate | 0.008 695 m potassium dihydrogen phosphate 0.030 43 m disodium hydrogen phosphate | 0.01 m borax | 0.025 m sodium bicarbonate 0.025 m sodium carbonate |
|---------------------|---|--|--|---|--|-----------------|--|
| 0 | _ | 3.863 | 4.003 | 6.984 | 7.534 | 9.464 | 10.317 |
| 5 | _ | 3.840 | 3.999 | 6.951 | 7.500 | 9.395 | 10.245 |
| 10 | - | 3.820 | 3.998 | 6.923 | 7.472 | 9.332 | 10.179 |
| 15 | - | 3.802 | 3.999 | 6.900 | 7.448 | 9.276 | 10.118 |
| 20 | - | 3.788 | 4.002 | 6.881 | 7.429 | 9.225 | 10.062 |
| 25 | 3.557 | 3.776 | 4.008 | 6.865 | 7.413 | 9.180 | 10.012 |
| 30 | 3.552 | 3.766 | 4.015 | 6.853 | 7.400 | 9.139 | 9.966 |
| 35 | 3.549 | 3.759 | 4.024 | 6.844 | 7.389 | 9.102 | 9.925 |
| 38 | 3.548 | - | 4.030 | 6.840 | 7.384 | 9.081 | |
| 40 | 3.547 | 3.753 | 4.035 | 6.838 | 7.380 | 9.068 | 9.889 |
| 45 | 3.547 | 3.750 | 4.047 | 6.834 | 7.373 | 9.038 | 9.856 |
| 50 | 3.549 | 3.749 | 4.060 | 6.833 | 7.367 | 9.011 | 9.828 |
| 55 | 3.554 | - | 4.075 | 6.834 | | 8.985 | _ |
| 60 | 3.560 | - | 4.091 | 6.836 | - | 8.962 | _ |
| 70 | 3.580 | - | 4.126 | 6.845 | - | 8.921 | - |
| 80 | 3.609 | - | 4.164 | 6.859 | - | 8.885 | - |
| 90 | 3.650 | - | 4.205 | 6.877 | _ | 8.850 | |
| 95 | 3.674 | _ | 4.227 | 6.886 | - | 8.833 | |

Id. at 130.

- 54. As illustrated, at the time of the alleged invention, a POSA would understand that a pH value, which must include at least one significant figure following the decimal point, would be subject to a maximum measurement error of ± 0.02 pH units.
- 55. The table from Harris, along with the other textbooks and evidence cited here, establish the sensitivity and accuracy of pH measurements as understood by a POSA at the time of the invention. Even before the 1991 date of Harris, the USP since 1985 has reported a precision of pH measurements to two decimal places and an accuracy/error of \pm 0.02 pH units.

VII. SPECIFIC OPINIONS REGARDING THE DISPUTED TERM

56. Earlier in this litigation, I considered the claims, specification and prosecution history from the perspective of a POSA. I understand that the Federal Circuit has instructed the

parties to focus on the extrinsic evidence, including the textbooks introduced by Plaintiff, and supporting extrinsic evidence such as this Declaration.

- 57. As noted, I understand that claims are to be interpreted as understood by a POSA at the relevant priority date.
 - A. A POSA Understands "a pH of 13" to Mean a pH Measurement Requiring at Least One Significant Digit and Subject to Routine Measurement Error
- 58. The claim language at issue is "a pH of 13 or higher," in the context of a "pharmaceutical composition . . . wherein said lyophilized pharmaceutical composition is [] formed from a bulk solution having a pH of 13 or higher." *See* the '802 patent at claim 1.
- 59. As discussed above, a POSA would understand that even though the pH value is written as "13," it is still referring to a specific pH value. As such, it will always carry an implied significant figure after the decimal place—at least one zero (most often two). By convention or for convenience, those zeros may be dropped in reporting pH values. Put simply, the POSA reading the claim term "a pH of 13" would understand it to mean either "13.0" or "13.00."
- 60. That opinion follows naturally from the information a pH value, by definition, conveys. In any measurement of ions expressed in exponential notation, there will always be at least a "1" multiplier: 1×10^{-13} . Otherwise, " 10^{-13} " would not be a pH value at all; it would be a bare power of ten. Because there is one significant figure in " 1×10^{-13} ," it necessarily implies one significant figure after the decimal in the equivalent pH value: pH of 13.0.
- 61. A POSA at the time of the invention would read "a pH of 13 or higher" to mean a pH of exactly 13.0 (or 13.00) or higher.
- 62. Should there be any deviation from a pH value of 13.0 (or 13.00), a POSA would understand that it would be subject to the stringent accuracy standards prevailing in the field of pharmaceutical sciences. In other words, at most, a POSA would understand a pH value to allow

for a maximum measurement error of ± 0.02 pH units. As shown in Harris, NSIT measured standardized pH values with an accuracy of ± 0.01 pH units. The USP has also long required pH meters to be accurate to within 0.02 pH units. USP 791 (2005), USP 791 (1995), USP 791 (1985).

- 63. The measurements outlined in Table 15-3 of Harris are consistent with a POSA's understanding of pH measurements as of the priority date. pH measurements, particularly in the pharmaceutical sciences, were precise down to the hundredth (two decimal places) or thousandth (three decimal places) with an accuracy of 0.02 (USP) or 0.01 (NIST) pH units.
- 64. This means that a "pH of 13" would extend to at most a pH of 12.98, using an error of ± 0.02 (USP). In no circumstance would a POSA understand a pH of 13 as claimed to allow a value as low as 12.5. Rather, a POSA would have been able to measure the pH of a solution accurately enough such that anything below 12.98 would not be considered a pH of 13. In other words, applying knowledge about pH values and how they are measured, a POSA would not consider anything below a pH of 12.98 to be "a pH of 13."
- 65. Likewise, a POSA would use the same level of precision for pH measurements, as stated in my Opinions Section above. Whether pH is reported as "2", "2.0," or "2.00", each measurement is understood to be capable of being measured down to the same precision.
- 66. My conclusion is both supported by the extrinsic evidence and consistent with the specification and prosecution history of the patents. ¹⁰ Understanding "pH of 13" to carry at least one implied significant digit makes sense of the following statement: "the pH of the bulk solution is preferably adjusted to about 12.5-13.5, most preferably 13, by the addition of sodium hydroxide." It is consistent with the POSA's understanding and makes sense to read "most

¹⁰ I understand that the '802 and '227 patents have similar specifications.

preferably 13" to mean 13.0; doing so places the most preferable embodiment in the middle of the range.

- 67. In Example 4 of the patents, Table 8 lists various formulations screened by the inventor, among them EPP-7, EPP-10, and EPP-13. The table specifies many reported pH values of 11, 12, and 13, as single integers; EPP-7, EPP-10, and EPP-13, for example, are listed with pH of "13." The text surrounding the table states that the inventor screened several formulations with the pH of the bulk solution for lyophilization adjusted between 10.5 and 13.0. See the '802 patent at col. 10:61-11:16 (Example 4; Table 8). This shows that the inventor equated "13" and "13.0." The March 20, 2006 provisional application confirms that this is correct: it states that the pH of the EPP-7, EPP-10, and EPP-13 formulations was "13.0." The necessarily implied significant figure of "0" was simply omitted in the Table that appears in the specification.
- 68. Example 5 shows that the inventor knew that pH could be measured to two decimal places (significant figures). It reports certain values of reconstituted epoprostenol with two significant figures. This reinforces that a POSA would understand the inventor to have applied a consistent level of precision across all testing—*i.e.*, at least to the tenth, but clearly to the hundredth of a pH unit.

B. A POSA Would *Not* Read a pH Value as an Order of Magnitude or Power of Ten, Nor Would a POSA Apply Whole Number Rounding

69. While the pH scale might appear to be linear, extending in its standard expression from 0(.00) to 14(.00) with neutral pH at 7(.00), the difference between each level on the pH scale is actually a 10-fold increase in hydrogen ion concentration. A solution with a pH of 1.0 is 10 times more acidic than a solution with a pH of 2.0. Likewise, a solution with a pH of 1.0 is 100 times

¹¹ See Patent Application 60/783,429, Specification at 3, 10 available at https://patentcenter.uspto.gov/applications/60783429/ifw/docs.

more acidic than a pH of 3.0. This passage from Kessel states the principle, while also demonstrating that "pH 3" for a POSA means the same thing as "pH 3.0":

Note that the hydrogen ion concentration changes by a multiple of 10 for every increase or decrease of one pH unit. For example, at pH 4.0, $[H^+_{(aq)}]$ is 1×10^{-4} mol/L; at pH 3.0, $[H^+_{(aq)}]$ is 1×10^{-3} mol/L. At pH 3, the $H^+_{(aq)}$ concentration is ten times higher.

Ex. B, Kessel 541.

- 70. I understand that Plaintiff has taken the position that "a pH of 13" would encompass values as low as 12.5 based on principles of rounding. This is not how a POSA would think about pH, in general or in the term "pH of 13 or higher." For one thing, because the pH scale is logarithmic, merely applying whole number rounding would introduce and allow for very large errors not standard in the pharmaceutical sciences. Put into pH terms, reading "pH of 13" to have an allowable error of 0.5 pH units on either side would provide a margin of error 50 times greater than the 0.01 pH unit NIST reference standard margin of error, or 25 times greater than the 0.02 pH unit in the USP expectation for pH meters.
- 71. A POSA would understand that standard pH meters are known and expected to measure to two decimal places, and that some pH meters measure pH values to the precision of one-thousandth (*i.e.*, three decimal places). No POSA would deviate from the precision and accuracy known to be standard in the field, as outlined by the USP and the NIST.
- 72. I further understand that Plaintiff has taken the position that a POSA will understand "pH of 13" to be equivalent to an order of magnitude or power of ten (10^{-13}) and would know based on non-pH rules of mathematics that they should round numbers in the exponent to reach the nearest power of ten $(e.g., 10^{-12.8})$ would round to 10^{-13} . I fundamentally disagree with this position.

73. As I have explained, pH values are not the same as powers of ten or orders of

magnitude. The claim term in this case is "pH of 13." Standing alone, a power of ten is not a pH

at all. For a pH value to be a pH value, at least one significant figure must be implied. Plaintiff's

textbooks repeatedly show this. They illustrate that pH of "13" equals 1 x 10⁻¹³. Because there is

one significant figure, the standalone digit "1," there must be one implicit significant figure after

"13," making it "13.0."

74. Furthermore, pH values are directly measured by pH meters and display pH

readings. A POSA would not read "pH of 13" to mean something other than a measurable pH

value of 13. And, as I have explained, a POSA will understand that measurements of pH in the

pharmaceutical sciences can and must be taken to a hundredths-place degree of precision, namely

with two significant figures.

75. For all the reasons outlined above, a POSA would not read the claim term a "pH of

13" and believe it to be an order of magnitude or power of ten subject to arithmetic rounding in

the exponent of the hydrogen ion concentration when it is expressed in scientific notation.

I declare under penalty of perjury that the foregoing is true and correct.

Dated: November 21, 2023

William T. Hensler, Ph.D.

EXHIBIT A

Pharmaceutical Subject Matter Expert William T. Hensler, Ph.D.

Years of Pharmaceutical Experience 25+

Education Ph.D. Chemical and Pharmaceutical Engineering. Rutgers

M.S. Chemical Engineering. Cornell University

B.S. Chemical Engineering. Rutgers

Summary of Relevant Qualifications Dr. William Hensler is a highly trained and experienced pharmaceutical engineer and subject matter expert with 25+ years of expertise in the development, manufacturing, technology transfer and process validation of FDA-regulated commercial pharmaceuticals in GMP facilities. His expertise includes:

- SME support for pharmaceutical case litigations involving patent disputes and infringements, breach of contract, analytical, facility and equipment issues and process validation
- Expertise in intellectual property analysis, evaluation and interpretation as it applies to patents and trade secrets of pharmaceutical processes, products and technologies
- Media and formulation development experience including phosphate buffered saline excipients
- Aseptic processing expertise and fill/finish of small and large volume parenterals and injectables including the inspection, labeling, packaging, storage and shipment of vials and syringes
- Expertise in calibration, maintenance, suitability and qualification (IQ/OQ/PQ) of analytical instruments for monitoring and testing pharmaceuticals such as osmometers, pH and conductivity instrumentation
- Experience in FDA Orange Book *Approved Drug Products with Therapeutic Equivalence* and investigation of NDAs and ANDAs
- Familiarity with ICH Guidelines including ICH Q2 (R1) Analytical Validation, Q3E Impurities, Q6A
 Specifications: Test Procedures and Acceptance Criteria for New Drug Substances and New Drug
 Products: Chemical Substances
- Extensive manufacturing expertise in cGMP bulk API and drug product (final dosage forms)
- Support for Commercial Supply Agreements and Quality Agreements, Tech Transfer Agreements
- Investigation and remediation of FDA 483s, Warning Letters and consent decrees
- Quality system evaluation (SOPs, CAPA, deviations, training, change management)

Pharmaceutical Development, Manufacturing and Process Validation Experience

Throughout his career, Dr. Hensler has been actively engaged in bulk API and secondary manufacturing of pharmaceuticals, including the development and scale up of processes for pharmaceutical products under cGMP according to FDA and ICH Guidelines. His expertise includes design of experiments (DOE), cGMP process design, critical process parameter and critical quality attribute identification and in-process and release specifications for pharmaceutical products.

He is skilled in the quality and regulatory aspects of new and existing pharmaceutical products, intellectual property evaluation, Type II DMFs and oversight of GMP manufacturing operations. He has expertise in all aspects of process validation including validation master plans, process performance qualifications, control parameter identification and report writing, technical transfer packages of drug substances and drug products.

His broad expertise includes the processes and unit operations which support aseptic bulk and secondary pharmaceutical manufacturing -= reactors, blenders, mixers, vessels, centrifuges, incubators, stability chambers, lyophilizers, filtration apparatus, homogenizers, liquid filling, as well as vial and syringe filling. He has worked for international pharmaceutical companies Sicor (now TEVA), Bristol-Myers Squibb, Merck, Schering-Plough, Pfizer, Sanofi and Astra Zeneca

Selected Manufacturing and Validation Experience

Sr. Vice President of Manufacturing Operations- Ology (Alachua, FL) Pharmaceutical executive responsible for the overall design, startup, validation, staffing and cGMP operation of a 180,000 square foot, \$250 MM bulk API contract manufacturer. Managed all equipment procurement and qualification activities, organized, hired and trained over 150 manufacturing, engineering and support staff. Brought facility to a successful state of readiness from conceptual design through equipment procurement, start-up and validation. Managed development operations of incoming new biologics and collaborated with analytical development to procure, commission and qualify analytical testing laboratories and procedures for in-process and release testing according to ICH Q2 (R1) Analytical Validation, Q3E Impurities and Q6A Specifications: Test Procedures and Acceptance Criteria for New Drug Substances and New Drug Products. Assisted in the establishment of the Quality Group and quality systems per ICH Q9 and Q10 Guidelines including manufacturing batch records, SOPs, equipment, facility and process validation protocols, established commercial supply agreements.

Principle Consultant - Sicor (now TEVA - Irvine, CA). Technical consultant for Mr. Carlo Salvo (former Board Member of TEVA) to assure successful startup and operational excellence of numerous bulk API and final dosage form facilities internationally, including sites in Lithuania, Italy, Mexico and California. Organized, planned and initiated projects for existing and new API and secondary manufacturing facilities which included batch and continuous lines. In this role, he also performed inspections and investigations, identified personnel staffing and training deficiencies and problems with equipment validation and out-of-spec products, performed corrective and preventative action (CAPA) according to ICH Guidelines, and implemented continuous improvement programs.

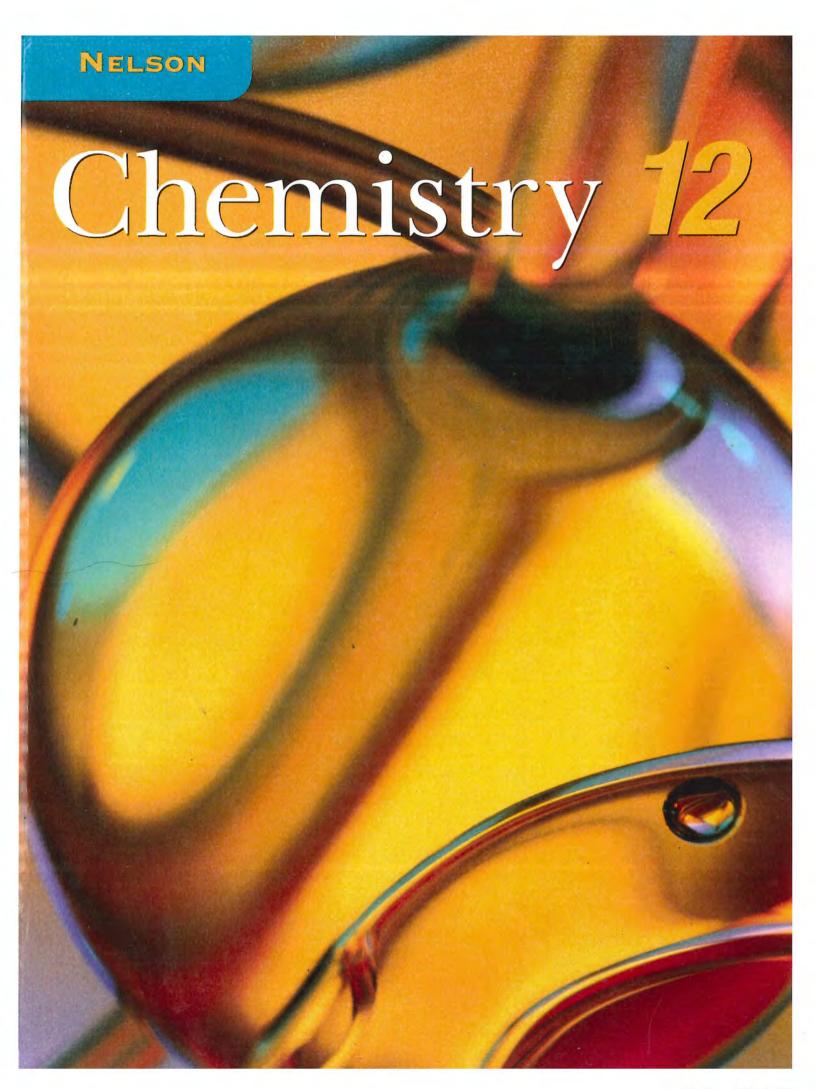
Bulk Manufacturing Manager - Merck & Company (formerly Schering-Plough, Union, NJ) Managed all cGMP development and manufacturing operations for Schering-Plough's alfa-2b interferon (bulk

API). Responsible for development of chemically-defined cell free media formulations using phosphate buffered saline and sodium bicarbonate excipients. Maintained qualification and calibration program for all in-process analytical instrument such as osmometers, pH and conductivity instruments, dissolved oxygen measurements, cell viability and analyte measurement devices. Managed day-to-day operations, batch planning and scheduling, meeting production quotas, training staff, process validation, annual FDA visits, writing and maintaining SOPs and batch records, and managing three shift operations staff of 60 operators, technicians, scientists and engineers.

Lead Validation Engineer - Bristol-Myers-Squibb (Hopewell, NJ) Development and process validation of monoclonal antibody and fusion proteins for BMS's pipeline of development biologics. Wrote validation master plan, validation protocols, executed IQ/OQ/PQ equipment protocols, remediated equipment problems and completed validation of equipment and facility. Followed up with process performance qualification (PPQ) of two cGMP products in development.

EXHIBIT B

Previously Filed as ECF No. 63, Exhibit 6



NELSON

Chemistry 12

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Printer

Transcontinental Printing Inc.

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Printed and bound in Canada 1 2 3 4 05 04 03 02

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National Library of Canada Cataloguing in Publication Data

Main entry under title: Nelson chemistry 12

Includes index. ISBN 0-17-625986-4

1. Chemistry. I. Jenkins, Frank, 1944-

QD33.N442 2002 540 C2002-900872-7

Acknowledgments

Nelson and the authors of Nelson Chemistry 12 thank the staff and, students of Mary Ward Catholic Secondary School and The Bishop Strachan School for the use of their facilities, and for the grace and generosity of their help.

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chapter

8

Acid-Base Eguilibrium

In this chapter, you will be able to

- compare strong and weak acids and bases using the concept of equilibrium;
- define equilibrium constant expressions, such as K_w, K_a, and K_b;
- use appropriate vocabulary to communicate ideas, procedures, and results related to acid-base systems;
- solve equilibrium problems involving K_a, K_b, pH, and pOH;
- predict, in qualitative terms, whether a solution of a specific salt will be acidic, basic, or neutral;
- solve problems involving acid-base titration data and the pH at the equivalence point;
- explain how buffering action affects our daily lives;
- describe the characteristics and components of a buffer solution.

Water is the most common liquid on Earth. It is found on the surface in lakes, rivers, and oceans; beneath the surface as ground water; and in the atmosphere as a vapour. The bodies of all living organisms are at least 66% water by mass. Water dissolves a wide range of ionic and polar substances, including table salt and table sugar, allowing for a huge variety of aqueous solutions. The most familiar of these solutions in the laboratory, workplace, and home are those of acids and bases. Vinegar, lemon juice, vitamin C, and battery fluid are common acidic solutions; drain cleaner, milk of magnesia, and household ammonia are common bases.

Living organisms are sensitive to the acidity of aqueous solutions in their internal and external environments. The pH of human blood must be kept at precisely 7.4. A sustained increase or decrease of only 0.2 pH units could mean death. How does the body maintain such a narrow range of pH when we consume so many acidic foods and beverages? We shall explore such concepts later in this chapter.

If the water in rivers and streams becomes even slightly acidic, trout and salmon will not survive. Soil pH is a prime determinant of the type of vegetation an area can support. Below a pH of 6, most plants absorb essential nutrients so poorly that growth is stunted and leaves turn yellow. Of course, there are exceptions — rhododendrons fail to thrive in soils with pH levels above 5.5.

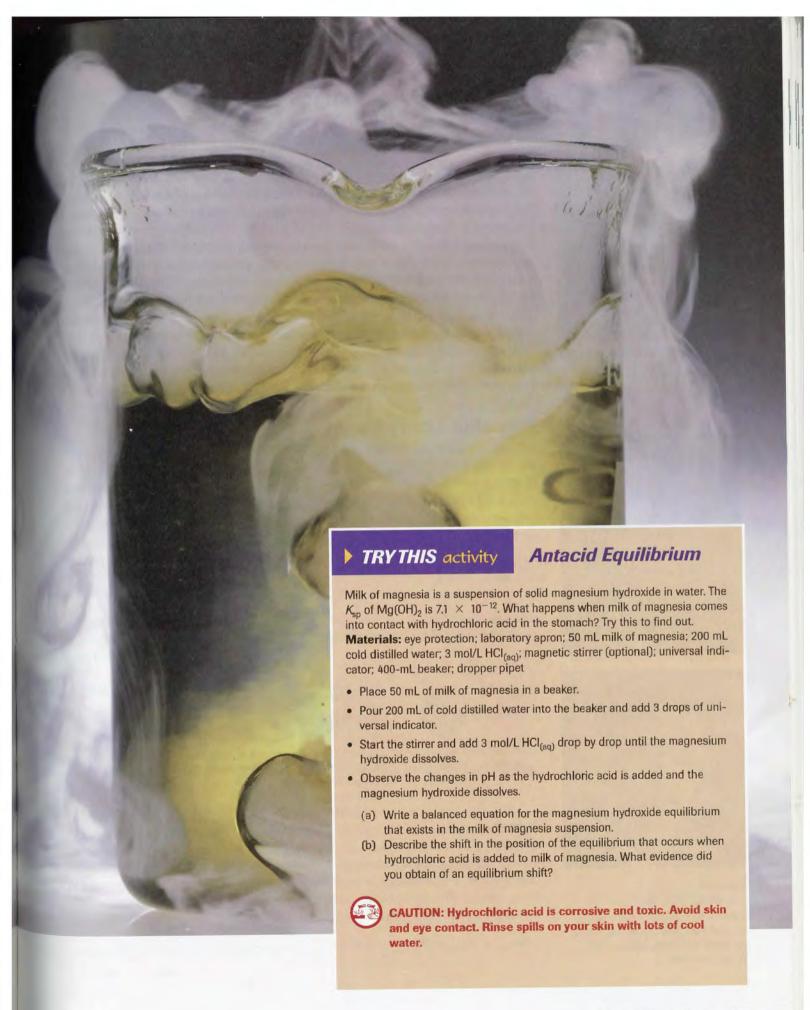
Acids and bases are extremely useful materials and in some cases essential to the proper functioning of natural and synthetic processes. Acids are used to etch glass and digest food. Bases are used as cleaning agents, rocket fuel, and dyes. Both are active ingredients in a host of pharmaceutical drugs. Aspirin, the world's most popular analgesic, is an acid. Morphine, a powerful painkiller, is a base.

REFLECT on your learning

- 1. Why is the pH of pure water at SATP equal to 7?
- 2. Solutions of acetic acid and hydrochloric acid of the same concentration are not equally acidic. Which of the two solutions has a lower pH? Why?
- 3. When equal amounts of the same concentrations of hydrochloric acid and sodium hydroxide are mixed, the resulting solution is neutral (pH = 7). When equal amounts of equal concentrations of acetic acid and sodium hydroxide are mixed, the resulting solution is basic (pH>7). Explain.
- 4. Most soft drinks are acidic solutions. When you consume a soft drink, acids are absorbed into the bloodstream. However, the pH of blood remains virtually unchanged. Why?

526 Chapter 8

NEL



8.1 The Nature of Acid-Base Equilibria

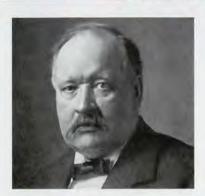


Figure 1 Svante Arrhenius (1859–1927)

Acids and bases are electrolytes that form aqueous solutions with unique properties. Acidic solutions like vinegar are sour tasting, conduct electricity, and turn blue litmus red. Basic solutions, like aqueous ammonia, also conduct electricity, are generally bitter tasting, feel slippery, and turn red litmus blue.

Svante Arrhenius (**Figure 1**), a Swedish chemist, was the first to characterize acids and bases in terms of their chemical properties. According to Arrhenius, acids are solutes that produce hydrogen ions, $H^+_{(aq)}$, in aqueous solutions, while bases produce hydroxide ions, $OH^-_{(aq)}$, when dissolved in water. This model adequately explains the properties of most acids and ionic hydroxide bases, but fails to satisfactorily account for the basic properties of compounds that do not contain the hydroxide ion, such as ammonia $(NH_{3(aq)})$.

In 1923, Johannes Brønsted of Denmark (**Figure 2(a)**) and Thomas Lowry of England (**Figure 2(b)**) recognized that, in most acid-base interactions, a proton (H⁺ ion) is transferred from one reactant to another.

Brønsted-Lowry Theory

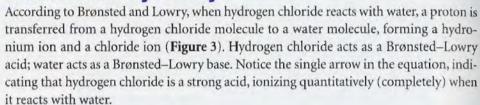






Figure 2
J. Brønsted (1879–1947) and T.
Lowry (1874–1936) independently
created new theoretical definitions
for acids and bases based upon
proton transfer.

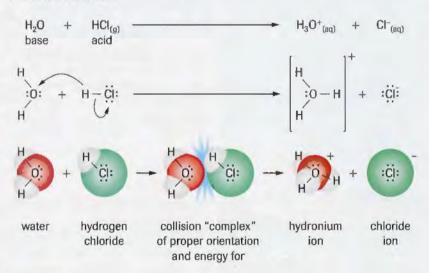


Figure 3

When ammonia reacts with water, a water molecule acts as a Brønsted–Lowry acid, donating a proton to ammonia, the Brønsted–Lowry base. Notice the double arrow in the equation, indicating that ammonia is a weak base, ionizing incompletely and forming a dynamic equilibrium with the products of the reaction.

$$NH_{3(g)} + H_2O_{(1)} \rightleftharpoons NH_{4(aq)}^+ + OH_{(aq)}^-$$

According to the Brønsted-Lowry concept,

- a Brønsted-Lowry acid is a proton donor, and
- a Brønsted-Lowry base is a proton acceptor.

A substance can be classified as a Brønsted-Lowry acid or base only for a specific reaction. This point is important - protons may be gained in a reaction with one substance, but lost in a reaction with another substance. (For example, in the reaction of HCl with water, water acts as a base, whereas in the reaction of NH3 with water, water acts as an acid.) A substance that appears to act as a Brønsted-Lowry acid in some reactions and as a Brønsted-Lowry base in other reactions is called amphoteric (amphiprotic).

In baking soda, the hydrogen carbonate ion, HCO₃⁻, is amphoteric, as shown by the following reactions.

The advantage of the Brønsted-Lowry definitions over the Arrhenius definitions is that they enable us to define acids and bases in terms of chemical reactions rather than simply as substances that form acidic and basic aqueous solutions. A definition of acids and bases in terms of chemical reactions allows us to describe, explain, and predict many reactions in aqueous solution, non-aqueous solution, or pure states. For example, according to Arrhenius, an acid-base neutralization produces water and a salt as in the reaction between sodium hydroxide and hydrochloric acid,

$$NaOH_{(aq)} + HCI_{(aq)} \rightarrow H_2O_{(l)} + NaCI_{(aq)}$$

However, when ammonia, a basic substance, reacts with hydrogen chloride, an acidic substance, a neutralization occurs (in the gas state) that does not involve hydronium ions, hydroxide ions, or water,

$$NH_{3(g)} + HCI_{(g)} \rightarrow NH_4CI_{(g)}$$

In this reaction, an H+ ion (a proton) transfers from the Cl atom in the HCl molecule to the N atom of the NH3 molecule.

According to the Brønsted-Lowry concept, acid-base reactions involve the transfer of a proton. These reactions are universally reversible and result in an acid-base equilibrium.

Reversible Acid-Base Reactions

In a proton transfer reaction at equilibrium, both forward and reverse reactions involve Brønsted-Lowry acids and bases. For example, in an acetic acid solution, we can describe the forward reaction as a proton transfer from acetic acid to water molecules and the reverse reaction as a proton transfer from hydronium to acetate ions.

$$\begin{array}{c|c} H^+ & \text{base} & \text{acid} \\ HC_2H_3O_{2(\text{aq})} + H_2O_{(1)} \rightleftharpoons C_2H_3O_{2(\text{aq})} + H_3O^+_{(\text{aq})} \\ \text{acid} & \text{base} & \\ \hline H^+ & \\ \end{array}$$

amphoteric (amphiprotic)

in the Brønsted-Lowry model, a substance capable of acting as an acid or a base in different chemical reactions; a substance that may donate or accept a proton.

DID YOU KNOW

Debatable Synonyms

The terms amphoteric and amphiprotic are commonly used as synonyms. However, there may be a difference. Amphoteric means "may act as an acid or a base" and amphiprotic means "may accept or donate protons." Since Brønsted-Lowry acids and bases are defined in terms of an entity's ability to accept or donate protons, an amphiprotic substance will always be amphoteric. However, in a more general model of acids and bases called the Lewis model (Section 8.3), acids and bases are defined according to an entity's ability to accept or donate a pair of electrons. In this case, an amphoteric substance may or may not be amphiprotic.

Acid-Base Equilibrium 529

LEARNING TIP

In organic chemistry (Chapters 1 and 2), and elsewhere in this book you will see the formula for acetic acid written CH3COOH(aq). This is done to emphasize that organic acids are carboxylic acids possessing the carboxyl group (-COOH). In this chapter, however, we will write the formulas for all acids, including carboxylic acids, with the ionizable hydrogen atoms written at the beginning of the formula, according to the nomenclature rules for writing acid formulas that you learned in a previous chemistry course. Thus, acetic acid (CH3COOH(aq)) is written HC₂H₃O_{2(aq)}, and oxalic acid (HOOCCOOH(aq)) is written H₂C₂O_{4(aq)}; their conjugate bases are $C_2H_3O_{2(aq)}$, and $C_2O_{4(aq)}$ respectively.

conjugate acid-base pair two substances whose formulas differ only by one H⁺ unit

LEARNING TIP

The conjugate acid always contains one more H⁺ than the conjugate base.

This equilibrium is typical of all Brønsted-Lowry acid—base reactions. There will always be two acids (in the above example, $HC_2H_3O_{2(aq)}$ and $H_3O_{(aq)}^+$) and two bases (in the above example, $H_2O_{(l)}$ and $C_2H_3O_{2(aq)}^-$) in any acid—base equilibrium. Furthermore, the base on the right ($C_2H_3O_{2(aq)}^-$) is formed by removal of a proton ($H_{(aq)}^+$ ion) from the acid on the left ($HC_2H_3O_{2(aq)}^-$). The acid on the right ($H_3O_{(aq)}^+$) is formed by the addition of a proton to the base on the left ($H_2O_{(l)}$). A pair of substances whose molecular formulas differ by a single H^+ ion (a proton) is called a **conjugate acid—base pair**. An acetic acid molecule and an acetate ion are a conjugate acid—base pair. Acetic acid is the conjugate acid of the acetate ion and the acetate ion is the conjugate base of acetic acid. The hydronium ion and water are the second conjugate acid—base pair in this equilibrium.

conjugate pair
$$HC_2H_3O_{2(aq)} + H_2O_{(1)} \rightleftharpoons C_2H_3O_{2(aq)} + H_3O^+_{(aq)}$$

$$conjugate pair$$

A Competition for Protons

The Brønsted–Lowry model of acids and bases allows us to view acid–base reactions as a competition for protons between two bases. For example, in the acetic acid equilibrium, the competition is between the acetate ion, $C_2H_3O_{2(aq)}$ and water, $H_2O_{(aq)}$.

$$H_2O_{(1)} \stackrel{\leftarrow}{\longrightarrow} H^* \stackrel{\rightarrow}{\longrightarrow} C_2H_3O_{2(aq)}$$

In a 0.1 mol/L solution of acetic acid, $HC_2H_3O_{2(aq)}$, at SATP, electrical conductivity measurements show that, at equilibrium, only about 1.3% of the $HC_2H_3O_{2(aq)}$ molecules have reacted with water to produce acetate ions and hydronium ions. It appears that the ability of the $C_2H_3O_2^-$ part of the $HC_2H_3O_2$ molecule to hold on to its proton (H^+ ion) is much greater than the ability of H_2O to pull the proton away. Therefore, the percent ionization is low. This may help explain why the following equilibrium lies far to the left, and why we call acetic acid a *weak* acid.

However, when HCl molecules react with H_2O , the chlorine atom in HCl has a much weaker affinity for the proton of the hydrogen atom it is bonded to than H_2O does. Thus, the water molecule wins the competition for HCl's proton, causing the H^+ ion to be completely transferred to H_2O , which becomes H_3O^+ . Virtually every HCl molecule loses this competition, which helps explain why the following equilibrium lies very far to the right (thus, the one-way arrow), and why we call HCl a *strong* acid.

99%
$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O_{(aq)}^+ + Cl_{(aq)}^-$$

In general, the terms strong acid and weak acid can be explained by the Brønsted-Lowry concept. Using $HA_{(aq)}$ as the general symbol for an acid and $A_{(aq)}^-$ as its conjugate base, we represent an acid ionization reaction as follows:

$$HA_{(aq)} + H_2O_{(1)} \rightleftharpoons H_3O_{(aq)}^+ + A_{(aq)}^-$$

The extent of the proton transfer between HA and H_2O determines the strength of $HA_{(aq)}$. In Brønsted–Lowry terms, when a strong acid reacts with water, the transfer of protons is virtually complete in the forward direction and almost no transfer of

protons occurs via the reverse reaction. In other words, the reaction of a strong acid with water is essentially 100% complete. The strongest acids have the highest percent reaction (or percent ionization). The forward reactions of these acids are strongly favoured. Weaker acids have lower percent reactions, so their equilibrium position is farther to the left, favouring the reactants rather than the products.

In terms of a competition for protons, a strong acid has a very low attraction for its proton and easily donates it to a base, even a relatively weak base like water. This leads to the interpretation that the conjugate base, A⁻, of a strong acid has a very weak attraction for protons: It is a very weak base. A useful generalization regarding the relative strengths of a conjugate acid—base pair is:

The stronger an acid, the weaker its conjugate base, and conversely, the weaker an acid, the stronger its conjugate base.

It is common to represent the equation for the ionization of an acid in water by abbreviating the ionization equation,

$$HA_{faq)} + H_2O_{(1)} \rightleftharpoons H_3O_{(aq)}^+ + A_{(aq)}^-$$

to

$$HA_{(aq)} \rightleftharpoons H_{(aq)}^+ + A_{(aq)}^-$$

For example,

$$HC_2H_3O_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_3O_{(aq)}^+ + C_2H_3O_{2(aq)}^-$$

reduces to

$$HC_2H_3O_{2(aq)} \rightleftharpoons H^+_{(aq)} + C_2H_3O_{2(aq)}$$

The abbreviated equation (bottom) is produced by removing the water molecule that is common to both sides of the complete equation (top). We will use the abbreviated form throughout this chapter. However, always keep in mind that, while it communicates the essential change that takes place in the reaction (the ionization of HA), it does not communicate the important role played by water in causing the acid to ionize, or the fact that the proton $(H_{(aq)}^+)$ most probably exists in solution as a hydronium ion, $H_3O_{(aq)}^+$.

SUMMARY

Brønsted-Lowry Definitions

- · An acid is a proton donor.
- · A base is a proton acceptor.
- An amphoteric substance is one that appears to act as a Brønsted–Lowry acid (a proton donor) in some reactions and as a Brønsted–Lowry base (a proton acceptor) in other reactions.
- A conjugate acid—base pair consists of two substances that differ only by a proton—the acid has one more proton than its conjugate base.

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- A strong acid has a very weak attraction for protons. A strong base has a very strong attraction for protons.
- The stronger an acid, the weaker its conjugate base, and conversely, the weaker an
 acid, the stronger its conjugate base.

Practice

Understanding Concepts

- Use the Brønsted-Lowry definitions to identify the two conjugate acid-base pairs in each of the following acid-base reactions.
 - (a) $HCO_{3(aq)}^{-} + S_{(aq)}^{2-} \rightleftharpoons HS_{(aq)}^{-} + CO_{3(aq)}^{2-}$
 - (b) $H_2CO_{3(aq)} + OH_{(aq)}^- \rightleftharpoons HCO_{3(aq)}^- + H_2O_{(1)}$
 - (c) $HSO_{4(aq)} + HPO_{4(aq)}^{2-} \Rightarrow H_2PO_{4(aq)}^{-} + SO_{4(aq)}^{2-}$
 - (d) $H_2O_{(1)} + H_2O_{(1)} \rightleftharpoons H_3O_{(8q)}^+ + OH_{(8q)}^-$
- 2. Identify all the amphoteric entities in question 1.
- Some ions can form more than one conjugate acid-base pair. List the two conjugate acid-base pairs involving a hydrogen carbonate ion in the reactions in question 1.

The Autoionization of Water

Water is never just a collection of H_2O molecules. Even a sample of contaminant-free water has a very slight conductivity that is observable if measured with very sensitive instruments. According to Arrhenius's theory, conductivity is due to the presence of ions. So, there must be ions in "pure" water. What is the nature of these ions, and what is their source? How many are there, and do their numbers change? Experiments have revealed that some water molecules react with each other to produce hydronium, $H_3O^+_{(aq)}$, and hydroxide, $OH^-_{(aq)}$, ions according to the following equation.

$$H_2O_{(1)} + H_2O_{(1)} \rightleftharpoons H_3O_{(aq)}^+ + OH_{(aq)}^-$$

Because the conductivity is so slight, there must be considerably more water molecules than ions in the equilibrium mixture at SATP. In every sample of water, an equilibrium is formed between hydronium ions, hydroxide ions, and water molecules that greatly favours the water molecules.

Of the billions of random collisions occurring among water molecules, a few are at the right energy and orientation to cause a reaction. This results in the transfer of a proton (H⁺ ion) from one molecule of water to the other, producing a hydronium ion, $H_3O_{(aq)}^+$, and a hydroxide ion, $OH_{(aq)}^-$ (Figure 4).

Figure 4

The collision that forms hydronium and hydroxide ions is very rare.

autoionization of water the reaction between two water molecules producing a hydronium ion and a hydroxide ion

This process is called the **autoionization of water**, since water molecules ionize one another. The H_3O^+ ion produced may be viewed as a water molecule, H_2O , with an H^+ ion (a proton) attached by a coordinate covalent bond to the oxygen atom. Chemists often omit the water molecule that carries the H^+ ion for convenience. In this way, the equilibrium may be written

$$H_2O_{(1)} \rightleftharpoons H_{(aq)}^+ + OH_{(aq)}^-$$

It is important to remember, however, that water molecules don't simply (or spontaneously) dissociate into H⁺ and OH⁻ ions, but rather, that the production of ions occurs as the result of an ionization process in which a proton is transferred from one molecule to another. Evidence indicates that fewer than two water molecules in one billion ionize at SATP.

The water equilibrium, like all chemical equilibria, obeys the law of mass action (equilibrium law). Therefore, we can construct an equilibrium law equation:

$$\frac{[H_{(aq)}^+][OH_{(aq)}^-]}{[H_2O_{(1)}]} = K$$

The concentration of water molecules in pure water and in dilute aqueous solutions is essentially constant and equal to 55.6 mol/L. This value is derived from the density and molar mass of water:

$$[H_2O_{(j)}] = \frac{1.00 \times 10^3 \text{ g/L}}{18 \text{ g/mol}}$$

= 55.6 mol/4

Therefore, a new constant, which incorporates both the constant value of $[H_2O_{(l)}]$ and the equilibrium constant, can be calculated. This new constant is called the **ion product constant for water**, K_w .

$$\begin{split} \frac{[H_{(aq)}^{+}][OH_{(aq)}^{-}]}{[H_{2}O_{(j)}]} &= & \mathcal{K} \\ [H_{(aq)}^{+}][OH_{(aq)}^{-}] &= & \mathcal{K}[H_{2}O_{(j)}] \\ & & \qquad \qquad \\ & & \qquad \\ & & \qquad \qquad \\ & & \qquad \qquad \\ & & \qquad \\ & \qquad \\$$

$$[H^{+}_{(aq)}][OH^{-}_{(aq)}] = K_{w}$$

The equilibrium equation for the autoionization of water shows that hydrogen ions and hydroxide ions are formed in a 1:1 ratio. Therefore, the concentrations of hydrogen ions and hydroxide ions in pure water must be equal. Precise measurements of pure water at 25°C show that the concentrations of $H_{(aq)}^+$ and $OH_{(aq)}^-$ are, in fact, the same: 1.0×10^{-7} mol/L.

$$[H_{(aq)}^+] = [OH_{(aq)}^-] = 1.0 \times 10^{-7} \text{ mol/L}$$

Therefore, at SATP

$$\begin{array}{lll} \textit{K}_{W} &=& [H_{(aq)}^{+}][OH_{(aq)}^{-}] \\ \textit{K}_{W} &=& (1.0 \times 10^{-7} \, mol/L)(1.0 \times 10^{-7} \, mol/L) \\ \textit{K}_{W} &=& 1.0 \times 10^{-14} \end{array}$$

As usual, we do not include units with the value of K_w . This will be the case with all equilibrium constants encountered in this chapter.

The autoionization of water takes place in *all* aqueous solutions. However, since acids and bases may be dissolved in water, the concentrations of $H^+_{(aq)}$ and $OH^-_{(aq)}$ ions may not be equal in all solutions. Dissolving acids increases $[H^+_{(aq)}]$ and dissolving bases increases $[OH^-_{(aq)}]$. Nevertheless, in all aqueous solutions at SATP, the product of the concentrations of $H^+_{(aq)}$ and $OH^-_{(aq)}$ is constant and equal to 1.0×10^{-14} , K_w .

ion product constant for water, $K_{\rm w}$ equilibrium constant for the ionization of water; 1.0×10^{-14}

LEARNING TIP

It is customary to write the value of $K_{\rm w}$ without units. However, note that it could be written as $1.0\times 10^{-14}~({\rm mol/L})^2$, allowing you to write concentrations calculated using $K_{\rm w}$ as mol/L.

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Table 1 Values of K_w at Selected Temperatures

| Temperature (°C) | K _w |
|---------------------|-----------------------|
| 0 | 1.5×10^{-15} |
| 10 | 3.0×10^{-15} |
| 20 | 6.8×10^{-15} |
| 25 | 1.0×10^{-14} |
| 30 | 1.5×10^{-14} |
| 40 | 3.0×10^{-14} |
| 50 | 5.5×10^{-14} |
| 60 | 9.5×10^{-14} |

In all aqueous solutions at SATP,
$$[H_{(aq)}^{+}][OH_{(aq)}^{-}] = K_{W} = 1.0 \times 10^{-14}$$

According to the Arrhenius theory, an acid is a substance that ionizes in water to produce hydrogen ions. The hydrogen ions provided by the acid increase the hydrogen ion concentration in the solution; the $[H^+_{(aq)}]$ will be greater than 10^{-7} mol/L at SATP, so the solution is *acidic*. A *basic* (or *alkaline*) solution is one in which the hydroxide ion concentration is greater than 10^{-7} mol/L at SATP, and a *neutral* solution is one where the hydrogen ion and hydroxide ion concentrations are the same and each equal to 10^{-7} mol/L at SATP.

A basic solution is produced, for example, by the dissociation, in water, of an ionic hydroxide such as sodium hydroxide.

| In neutral solutions | $[H_{(aq)}^+] = [OH_{(aq)}^-]$ |
|----------------------|--------------------------------|
| In acidic solutions | $[H_{(aq)}^+] > [OH_{(aq)}^-]$ |
| In basic solutions | $[H_{(aq)}^+] < [OH_{(aq)}^-]$ |

strong acid an acid that is assumed to ionize quantitatively (completely) in aqueous solution (percent ionization is > .99%) Another important point is that the numerical value given above for K_w is valid at SATP, but *not* at temperatures that are much higher or lower (**Table 1**). Recall that the value of any equilibrium constant depends on temperature. For higher temperatures, K_w has a greater value, so products are more favoured. This means that more water molecules become ionized in aqueous systems when the molecular collisions are more energetic and more frequent.

We can use the ion product constant for water, K_w , to calculate either the hydrogen ion concentration or the hydroxide ion concentration in an aqueous solution of a strong or weak acid or base at SATP, if the other concentration is known.

Since
$$K_{w} = [H_{(aq)}^{+}][OH_{(aq)}^{-}]$$

then $[H_{(aq)}^{+}] = \frac{K_{w}}{[OH_{(aq)}^{-}]}$
and $[OH_{(aq)}^{-}] = \frac{K_{w}}{[H_{(aq)}^{+}]}$

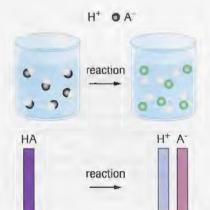


Figure 5 Strong acids ionize greater than 99% in aqueous solution.

Strong Acids

A **strong acid** is an acid that ionizes quantitatively (completely) in water to form hydrogen ions. The percent ionization of strong acids is greater than 99%. However, we will assume that it is 100% in calculations. For example, we will assume that every molecule of $HCl_{(g)}$ that dissolves in water ionizes into $H^+_{(aq)}$ and $Cl^-_{(aq)}$.

$$HCl_{(g)} \xrightarrow{H_2O_{(g)}} H_{(eq)}^+ + Cl_{(eq)}^-$$

This means that, although the label on a bottle of hydrochloric acid may say 1.0 mol/L $HCl_{(aq)}$, we assume that the solution contains virtually no HCl molecules (**Figure 5**). Instead, we assume that it contains 1.0 mol/L $H^+_{(aq)}$ and 1.0 mol/L $Cl^-_{(aq)}$ ions only. Container labels usually indicate the concentration of the substance(s) used to make the solution and do not usually describe the concentration(s) of the substances that form from the ionization (or dissociation) of the starting material.

There are relatively few strong acids: hydrochloric acid, HCl(aq), hydrobromic acid, HBr_(aq), sulfuric acid, H₂SO_{4(aq)}, nitric acid, HNO_{3(aq)}, and phosphoric acid, H₃PO_{4(aq)}, are the most familiar. **Monoprotic acids** like $HCl_{(aq)}$ contain only one ionizable "acidic" hydrogen atom. Diprotic acids like $H_2SO_{4(aq)}$ have two ionizable hydrogen atoms and triprotic acids like H₃PO_{4(aq)} have three. As with almost all acids, the ionizable hydrogen atoms of oxyacids such as sulfuric acid, nitric acid, and phosphoric acid are written first in the molecular formulas, but this does not necessarily give a clue to the structure of the molecule. In these molecules, the hydrogens are not attached to the sulfur, nitrogen, or phosphorous atoms but to oxygen atoms (Figure 6).

monoprotic acid an acid that possesses only one ionizable (acidic) proton



sulfuric acid. H2SO4(aq)



nitric acid HNO_{3(aq)}



phosphoric acid. H₃PO₄₍₈₀₎

Figure 6

The ionizable "acidic" hydrogen atoms of common oxyacids are covalently bonded to oxygen atoms.

We can now use two concepts—the assumption that strong acids ionize quantitatively in solution, and the value of Kw-to calculate the hydrogen ion or hydroxide ion concentrations of strong acid solutions.

Calculating $[OH^{-}_{(aq)}]$ or $[H^{+}_{(aq)}]$ of a Strong Acid

A 0.15 mol/L solution of hydrochloric acid at SATP is found to have a hydrogen ion concentration of 0.15 mol/L. Calculate the concentration of the hydroxide ions.

When analyzing problems dealing with equilibrium solutions of acids and bases, we must account for all of the entities that may contribute to the solution's hydrogen ion and hydroxide ion concentrations, since these give rise to the acid/base properties of the solution. After identifying all of the entities that may affect the acid-base balance, we must determine the major entities (solution components that are present in relatively large amounts). In most cases, a major entity determines the acid-base properties of the solution, and the minor entities may be ignored.

Since hydrochloric acid is a strong acid, we assume that it undergoes 100% ionization in aqueous solution.

Therefore, a 0.15 mol/L $HCl_{(aq)}$ solution will have 0.15 mol/L $H^+_{(aq)}$, and 0.15 mol/L $Cl^-_{(aq)}$. Water is a very weak electrolyte. It ionizes very little, according to the following equilibrium.

$$H_2O_{(1)} \rightleftharpoons H_{(aq)}^+ + OH_{(aq)}^-$$

In pure water,

$$[H_{(aq)}^+] = 1.0 \times 10^{-7} \text{ mol/L}$$
 and $[OH_{(aq)}^-] = 1.0 \times 10^{-7} \text{ mol/L}$

However, in an $HCl_{(aq)}$ solution, the $[H^+_{(aq)}]$ and $[OH^-_{(aq)}]$ contributed by the autoionization of water will be less than 1.0 imes 10 $^{-7}$ mol/L because the $H_{(aq)}^+$ ions produced by the ionization of HCl cause the water equilibrium to shift to the left (by Le Châtelier's principle), reducing the contribution of $H_{(aq)}^+$ ions (and $OH_{(aq)}^-$) from the autoionization of water to less

SAMPLE problem

LEARNING TIP

Unless stated otherwise, conditions in problems in this chapter are SATP.

than 1.0 \times 10⁻⁷ mol/L. Compared to the 0.15 mol/L $H_{(aq)}^+$ contributed by HCl, the tiny contribution made by the autoionization of water may be safely ignored. In a similar way, the miniscule contribution of OH_(aq) made by the autoionization of water may also be ignored. Therefore, the major entities in solution are

$$H_{(aq)}^+$$
 and $CI_{(aq)}^-$
(from HCI) (from HCI)

As indicated earlier, the concentration of chloride ions, $Cl_{(aq)}^-$, in this solution is 0.15 mol/L. This is a significant concentration. However, we may assume that this ion does not contribute to $[H_{(aq)}^+]$ or $[OH_{(aq)}^-]$ in the solution because it is the conjugate base of a strong acid. (Remember that the conjugate base of a strong acid is sufficiently weak for us to ignore its presence. We may assume this for the conjugate bases of all strong acids.) Therefore, in this problem, the major entity affecting the acid-base characteristics of the solution is the $H_{(aq)}^+$ ion produced by the ionization of HCI.

Since HCI(aq) ionizes quantitatively,

$$[H_{(aq)}^+] = 0.15 \text{ mol/L}$$

Now, use the K_w expression to calculate the concentration of hydroxide ions. (Remember that $K_{\rm w} = 1.0 \times 10^{-14}$ at SATP.)

$$K_{w} = [H_{(aq)}^{+}][OH_{(aq)}^{-}]$$

$$[OH_{(aq)}^{-}] = \frac{K_{w}}{[H_{(aq)}^{+}]}$$

$$= \frac{1.0 \times 10^{-14}}{0.15}$$

$$[OH_{(aq)}^{-}] = 6.7 \times 10^{-14} \text{ mol/L}$$

Always remember that, while we omit units in the Kw expression, we must always write units with concentration values in the solution.

Calculate the hydroxide ion concentration in a 0.25 mol/L HBr_(aq) solution.

Solution

Hydrobromic acid is a strong acid.

$$HBr_{(aq)} \longrightarrow H^{+}_{(aq)} + Br^{-}_{(aq)}$$

The major entities in solution are $H^+_{(aq)}$, $Br^-_{(aq)}$, and $H_2O_{(j)}$. We can ignore the insignificant amount of $OH^-_{(aq)}$ produced by the autoionization of water and the presence of Br_(aq) (a very weak base).

$$\begin{split} [H_{(aq)}^{+}] &= 0.25 \text{ mol/L} \\ K_w &= [H_{(aq)}^{+}][OH_{(aq)}^{-}] \\ [OH_{(aq)}^{-}] &= \frac{K_w}{[H_{(aq)}^{+}]} \\ &= \frac{1.00 \times 10^{-14}}{0.25} \\ [OH_{(aq)}^{-}] &= 4.0 \times 10^{-14} \text{ mol/L} \end{split}$$

Practice

Understanding Concepts

- 4. In a 0.30 mol/L HNO_{3(aq)} solution,
 - (a) what is the concentration of nitric acid molecules?
 - (b) what is the hydroxide ion concentration?
- Calculate the hydroxide ion concentration in a solution prepared by dissolving 0.37 g of hydrogen chloride in water to form 250 mL of solution.
- 6. The hydrogen ion concentration in an industrial effluent is 4.40 mmol/L (4.40 × 10⁻³ mol/L). Calculate the concentration of hydroxide ions in the effluent.

Applying Inquiry Skills

7. In a particular solution, chromate ions are in equilibrium with dichromate ions (Figure 7).

$$2 \operatorname{CrO}_{4(aq)}^{2-} + 2 \operatorname{H}_{(aq)}^{+} \rightleftharpoons \operatorname{Cr}_{2} \operatorname{O}_{7(aq)}^{2-} + \operatorname{H}_{2} \operatorname{O}_{(l)}$$

The equilibrium concentration of CrO_{4(aq)} depends on the acidity of the solution. Complete the Prediction and Experimental Design (including diagnostic tests) of the investigation report.

Question

How does a change in the hydrogen ion concentration affect the chromate-dichromate equilibrium?



Figure 7

In aqueous solution, chromate ions, CrO_{4 (aq)}, produce a yellow colour; dichromate ions, Cr₂O_{7(aq)}, produce an orange colour.

Answers

- 4. (a) 0 mol/L
 - (b) $3.3 \times 10^{-14} \text{ mol/L}$
- 5. 2.5×10^{-13} mol/L
- 6. 2.3×10^{-12} mol/L

Strong Bases

According to Arrhenius, a base is a substance that dissociates to increase the hydroxide ion concentration of a solution. Ionic hydroxides have varying solubility in water, but all are **strong bases** that dissociate quantitatively (completely) when they dissolve in water.

All of the hydroxides of Group 1 elements (LiOH(s), NaOH(s), KOH(s), RbOH(s), and $CsOH_{(s)}$) are strong bases. When these bases dissolve in water, one mole of hydroxide ion is produced for every mole of metal hydroxide that dissolves. For example,

These metal hydroxides are all highly soluble in water.

Group 2 elements form the strong hydroxides $Mg(OH)_{2(s)}$, $Ca(OH)_{2(s)}$, $Ba(OH)_{2(s)}$, and Sr(OH)2(s). When these bases dissolve in water, two moles of hydroxide ion are formed for every mole of metal hydroxide that dissolves in solution.

$$Ba(OH)_{2(s)} \xrightarrow{100\%} Ba_{(aq)}^{2+} + 2 OH_{(aq)}^{-}$$

$$H_2O_{(1)}$$

You may recall from Chapter 7 that these hydroxides are only slightly soluble in water. Their low solubility makes them useful in medical applications. Many antacids are suspensions of metal hydroxides in water, such as magnesium hydroxide in milk of magnesia. strong base an ionic substance that (according to the Arrhenius definition) dissociates completely in water to release hydroxide ions

Their low solubility prevents large hydroxide ion concentrations that could damage the tissues of the mouth and esophagus as the suspension is being ingested. Once in the stomach, the hydroxide ions react with the hydrogen ions in stomach acid, shifting the equilibrium to the right, and causing the undissolved salts to dissolve and produce higher (more effective) $OH_{(aq)}^-$ ion concentrations.

Just as we did with acids, we can now use two concepts — the assumption that strong bases dissociate quantitatively in solution and the value of $K_{\rm w}$ — to calculate the hydrogen ion or hydroxide ion concentrations of solutions of strong bases.

SAMPLE problem



Figure 8
Barium hydroxide has many uses, including in the refining of sugar.

Calculating $[H_{(aq)}^+]$ and $[OH_{(aq)}^-]$ of a Strong Base

 Calculate the hydrogen ion concentration in a 0.25 mol/L solution of barium hydroxide, a strong base (Figure 8).

We analyze problems involving strong bases in the same way we analyzed problems associated with strong acids.

First, we must identify the major entities in solution.

Begin by writing the dissociation equation for barium hydroxide in water:

The major entities are Ba_(aq), OH_(aq), and H₂O_(j).

Since $Ba(OH)_{2(aq)}$ is a strong base, we assume that it dissociates quantitatively (completely) into ions. From the balanced equation, we note that every mole of $Ba(OH)_2$ that dissociates produces one mole of $Ba_{(aq)}^{2+}$ and *two* moles of $OH_{(aq)}^{-}$.

Therefore,

$$[OH^{-}_{(aq)}] = 2(0.25 \text{ mol/L})$$

 $[OH^{-}_{(aq)}] = 0.50 \text{ mol/L}$

The autoionization of water also produces $OH^-_{(aq)}$ ions. However, since the concentration of $OH^-_{(aq)}$ contributed by this process $(1.0 \times 10^{-7} \text{ mol/L})$ is insignificant when compared to the 0.50 mol/L produced by the dissociation of $Ba(OH)_2$, it may be ignored. Also, since $Ba(OH)_2$ is a strong base, you may assume that the $Ba^{2+}_{(aq)}$ ions do not affect the acid-base properties of the solution. The $Ba^{2+}_{(aq)}$ ions have no affinity for $H^+_{(aq)}$ ions, nor can they produce $H^+_{(aq)}$ ions; they do not attract $OH^-_{(aq)}$ ions, nor can they produce $OH^-_{(aq)}$ ions. In general, you may ignore the presence of the cations of all ionic hydroxides when determining the acid-base properties of their aqueous solutions. This includes all Group 1 and 2 cations. However, in Section 8.3 you will learn that this assumption cannot be made for *all* dissolved metal cations.

Now use the K_w expression to calculate $[H_{(aq)}^+]$:

$$\begin{array}{lll} \textit{K}_{w} & = & [\textit{H}_{(aq)}^{+}][\textit{OH}_{(aq)}^{-}] \\ \\ [\textit{H}_{(aq)}^{+}] & = & \frac{\textit{K}_{w}}{[\textit{OH}_{(aq)}^{-}]} \\ \\ [\textit{H}_{(aq)}^{+}] & = & \frac{1.00 \times 10^{-14}}{0.50} \\ \\ [\textit{H}_{(an)}^{+}] & = & 2.00 \times 10^{-14} \, \text{mol/L} \end{array}$$

The concentration of hydrogen ions in the barium hydroxide solutions is 2.00 \times 10 $^{-14}$ mol/L.

Determine the hydrogen ion and hydroxide ion concentrations in 500 mL of an aqueous solution containing 2.6 g of dissolved sodium hydroxide.

As usual, we begin by writing a balanced equation for the dissolution of the strong base and use it to identify the major entities in solution.

$$NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$$

The major entities in solution are $Na_{(aq)}^+$, $OH_{(aq)}^-$, and $H_2O_{(1)}$. In this case, we are not given $[NaOH_{(aq)}]$. However, we are given the mass of $NaOH_{(s)}$ and the volume of the solution. We can use these quantities to calculate the concentration of the base immediately before dissociation.

$$NaOH_{(aq)} \rightarrow Na_{(aq)}^{+} + OH_{(aq)}^{-}$$

$$[NaOH_{(aq)}] = 2.6 \text{ g/500 mL}$$

$$m_{\text{NaOH}} = 2.6 \, \text{g}$$

$$M_{NaOH} = 40.00 \text{ g/mol}$$

$$n_{NaOH} = ?$$

First, convert the [NaOH_(aq)] from units of g/mL to units of mol/L.

$$n_{\text{NaOH}} = 2.6 \text{ g} \times \frac{1 \text{ mol}}{40.00 \text{ g}}$$

$$n_{\text{NaOH}} = 0.065 \, \text{mol}$$

[NaOH] =
$$\frac{0.065 \text{ mol}}{0.500 \text{ L}}$$

$$[NaOH] = 0.13 \text{ mol/L}$$

From the balanced equation, we note that every mole of NaOH dissociates into one mole of Na⁺_(aq) and one mole of OH⁻_(aq).

Therefore, after dissolution,

$$[OH_{(aq)}^{-}] = 0.13 \text{ mol/L}$$

We note that the concentration of $OH_{(aq)}^-$ produced by the autoionization of water is insignificant when compared to the 0.13 mol/L produced by the dissociation of NaOH. We also assume that since NaOH is a strong base, Na_(aq) does not affect the acid-base prop-

Now we can use the K_w expression to calculate the $[H_{(aq)}^+]$, assuming that $[OH_{(aq)}^{-} = 0.13 \text{ mol/L}.$

$$K_{\mathbf{w}} = [H_{(aq)}^+][OH_{(aq)}^-]$$

$$[H_{(aq)}^{+}] = \frac{N_{w}}{[OH_{(aq)}^{-}]}$$
$$= \frac{1.0 \times 10^{-14}}{0.13}$$

$$[H_{(aq)}^{+}] = 7.7 \times 10^{-14} \, \text{mol/L}$$

Therefore, the $[OH^-_{(aq)}]$ is 0.13 mol/L, and the $[H^+_{(aq)}]$ is 7.7 \times 10⁻¹⁴ mol/L.

Example

A cleaning solution contains 5.00 g of $KOH_{(aq)}$ in 2.00 L of solution. Calculate the $[H_{(aq)}^+]$ of the cleaning solution.

Solution

$$KOH_{(aq)} \longrightarrow K_{(aq)}^+ + OH_{(aq)}^-$$

The major entities are K_(aq), OH_(aq) and H₂O_(j).

$$n_{\text{KOH}} = 5.00 \text{ g} \times \frac{1.00 \text{ mol}}{56.11 \text{ g}}$$

$$n_{\text{KOH}} = 0.089 \, \text{mol}$$

$$[KOH_{(aq)}] = \frac{0.089 \text{ mol}}{2.00 \text{ L}}$$

$$[KOH_{(aq)}] = 4.46 \times 10^{-2} \text{ mol/L}$$

Since one mole of KOH dissociates into one mole of $K_{(aq)}^+$ and one mole of $OH_{(aq)}^-$,

$$[OH_{(aq)}^{-}] = 4.46 \times 10^{-2} \text{ mol/L}$$

Ignoring the $[OH_{(aq)}^-]$ produced by the autoionization of water, and $K_{(aq)}^+$,

$$K_{w} = [H_{(aq)}^{+}][OH_{(aq)}^{-}]$$

$$[H_{(aq)}^+] \ = \ \frac{{\it K}_{w}}{[OH_{(aq)}^-]}$$

$$= \frac{1.00 \times 10^{-14}}{4.46 \times 10^{-2}}$$

$$[H_{(aq)}^+] = 2.24 \times 10^{-13} \,\text{mol/L}$$

The concentration of hydrogen ions in the solution is 2.24×10^{-13} mol/L.

Answers

- 8. 7.2×10^{-13} mol/L
- 9. 3.34×10^{-14} mol/L
- 10. $1.40 \times 10^{-14} \text{ mol/L}$
- 11. 10-5%

Practice

Understanding Concepts

- Calculate the hydrogen ion concentration in a saturated solution of calcium hydroxide (limewater). Calcium hydroxide has a solubility of 6.9 mmol per litre of solution.
- The hydroxide ion concentration in a household cleaning solution is 0.299 mmol/L. Calculate the hydrogen ion concentration in the cleaning solution.
- 10. What is the hydrogen ion concentration in a solution made by dissolving 20.0 g of potassium hydroxide in water to form 500 mL of solution?
- 11. Calculate the percent ionization of water at SATP. Recall that 1,000 L of water has a mass of 1000 g.

Hydrogen Ion Concentration and pH

A concentrated acid solution may have a hydrogen ion concentration exceeding 10 mol/L. A concentrated base solution may have a hydrogen ion concentration of 10^{-15} mol/L , or less. Similarly, the hydroxide ion concentration can vary widely. Because of the tremendous range of hydrogen ion and hydroxide ion concentrations, scientists rely on a simple system for communicating concentrations. This system, called the pH scale, was developed in 1909 by Danish chemist Sören Sörenson. Expressed as a numerical value without units, the **pH** of a solution is the negative of the logarithm to the base ten of the hydrogen ion concentration.

$$pH = -log[H_{(aq)}^+]$$

pH values can be calculated from the hydrogen ion concentration. As shown in the following example, the digits preceding the decimal point in a pH value are determined

by the digits in the exponent of the given hydrogen ion concentration. These digits serve to locate the position of the decimal point in the concentration value and have no connection with the certainty of the value. However, the number of digits following the decimal point in the pH value is equal to the number of significant digits in the hydrogen ion concentration. For example, a hydrogen ion concentration of 2.7×10^{-3} mol/L corresponds to a pH of 2.57. (Two significant digits in the value for $[H^+_{(aq)}]$ means we should give the pH value to two decimal places.)

Example

Calculate the pH of a solution with a hydrogen ion concentration of 4.7×10^{-11} mol/L.

Solution

```
pH = -\log[H_{(aq)}^{+}]
= -\log(4.7 \times 10^{-11}) (two significant digits)
= 10.33 (two digits following the decimal point)
```

The solution has a pH of 10.33.

In pure water, and in any neutral solution at SATP, the concentrations of hydrogen and hydroxide ions are equal, and therefore the pH is 7.00:

$$\begin{split} [H^+_{(aq)}][OH^-_{(aq)}] &= 1.0 \times 10^{-14} \text{ mol/L} \\ [H^+_{(aq)}] &= [OH^-_{(aq)}] \\ [H^+_{(aq)}]^2 &= 1.0 \times 10^{-14} \\ [H^+_{(aq)}] &= \sqrt{1.0 \times 10^{-14} \text{ mol/L}} \\ [H^+_{(aq)}] &= 1.0 \times 10^{-7} \text{ mol/L} \\ pH &= -log (1.0 \times 10^{-7}) \\ pH &= 7.00 \end{split}$$

At SATP, an acidic solution is one in which the $[H_{(aq)}^+]$ is greater than 10^{-7} mol/L, a basic solution is one where $[H_{(aq)}^+]$ is less than 10^{-7} mol/L, and a neutral solution is one where $[H_{(aq)}^+]$ is equal to 10^{-7} mol/L. At SATP:

```
neutral solution pH = 7.00
acidic solution pH < 7.00
basic solution pH > 7.00
```

Note that the hydrogen ion concentration changes by a multiple of 10 for every increase or decrease of one pH unit. For example, at pH 4.0, $[H^+_{(aq)}]$ is 1×10^{-4} mol/L; at pH 3.0, $[H^+_{(aq)}]$ is 1×10^{-3} mol/L. At pH 3, the $H^+_{(aq)}$ concentration is ten times higher.

If pH is measured in an acid-base experiment, a conversion from pH to the molar concentration of hydrogen ions may be necessary. This conversion is based on the mathematical concept that a base ten logarithm represents an exponent.

$$[H_{(aq)}^+] = 10^{-pH}$$

The method of calculating the hydrogen ion concentration from the pH value is shown in the following example.

On many calculator

On many calculators, $-\log(4.7 \times 10^{-11})$ may be entered by pushing the following sequence of keys.



Note that, on some calculators, the EXP button may be labelled EE. Nevertheless, the sequence of keys remains the same. If your calculator lacks either of these keys, consult the user's manual for instructions.

LEARNING TIP

Notice that the negative sign in the definition of pH establishes an inverse relationship between the magnitude of the hydrogen ion concentration and the magnitude of the pH value.

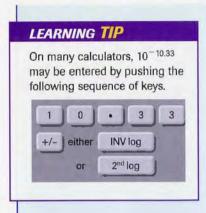
small pH value = large value of

[H_(aq)]

large pH value = small value of

[H⁺_(aq)]

Acid-Base Equilibrium 541



Example

Convert a pH of 10.33 to a hydrogen ion concentration.

Solution

$$\begin{array}{ll} [H^+_{(aq)}] &=& 10^{-pH} \\ &=& 10^{-10.33} \ mol/L \\ [H^+_{(aq)}] &=& 4.7 \ \times \ 10^{-11} \ mol/L \end{array} \qquad \mbox{(two digits following the decimal point)}$$

pOH and pK_w

The concentration of hydroxide ions is very small in dilute basic solutions. Therefore, it is convenient to describe hydroxide ion concentrations in a similar way as is done for $H^+_{(aq)}$ concentrations, by calculating **pOH**.

$$pOH = -log[OH_{(aq)}^-]$$

A solution's pOH may be used to calculate the hydroxide ion concentration:

$$[OH^{-}_{(aq)}] = 10^{-pOH}$$

The following example shows how the pOH of a solution is calculated from the $[OH_{(aq)}^-]$.

Example

Calculate the pOH of a solution with a hydroxide ion concentration of 3.0×10^{-6} mol/L.

Solution

$$pOH = -log[OH_{(aq)}^{-}]$$

= $-log(3.0 \times 10^{-6})$
 $pOH = 5.52$

The pOH of the solution is 5.52.

The mathematics of logarithms allows us to derive a simple relationship between pH and pOH. We derive this relationship below. However, before we do, we need to define a quantity, pK_w .

$$pK_w = -\log K_w$$

The numerical value of p K_w follows from the value of K_w , which is always 1×10^{-14} at SATP.

$$pK_w = -\log (1 \times 10^{-14})$$

= -(-14.00)
 $pK_w = 14.00$ (at SATP)

According to the rules of logarithms,

$$log(ab) = log(a) + log(b)$$

Using the equilibrium law expression for the autoionization of water,

$$\begin{split} [H^+_{(aq)}][OH^-_{(aq)}] &= \mathcal{K}_w \\ log([H^+_{(aq)}][OH^-_{(aq)}]) &= log(\mathcal{K}_w) \\ log[H^+_{(aq)}] &+ log[OH^-_{(aq)}] &= log(\mathcal{K}_w) \\ (-log[H^+_{(aq)}]) &+ (-log[OH^-_{(aq)}]) &= -log(\mathcal{K}_w) \\ \end{split}$$
 or
$$pH + pOH = p\mathcal{K}_w \\ and therefore pH + pOH = 14.00 \qquad (at SATP) \end{split}$$

This relationship enables a quick conversion between pH and pOH.



Figure 9

Purple cabbage boiled in water produces an extract that changes colour in different solutions. The test tubes show the colour of the cabbage juice in solutions of (from left) a strong acid (pH 1), a weak acid (pH 4), a neutral solution (pH 7), a weak base (pH 9), and a strong base (pH 14). All concentrations are 0.10 mol/L.

Example

What is the pOH of a solution whose pH is measured to be 6.4?

Solution

$$pH + pOH = 14$$

 $pOH = 14 - pH$
 $= 14 - 6.4$
 $pOH = 7.6$

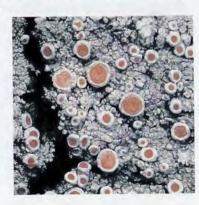
The pOH of the solution is 7.6.

Measuring pH

There are several different ways of measuring the pH of a solution, some more precise than others. Many plant compounds and synthetic dyes change colour when mixed with an acid or a base (**Figure 9**).

Substances that change colour when they react with acids or bases are known as **acid-base indicators**. A common indicator used in school laboratories is litmus, a dye obtained from a lichen (**Figure 10**). It is prepared by soaking absorbent paper in litmus solution and then drying it. As you know, red and blue are the two colours of the litmus

dye. Litmus dye is red below pH 4.7 and blue above pH 8.3. The colour change occurs over this pH range. Litmus remains brown at approximately pH 6.5, which is very close to neutral pH. A solution is acidic if it causes blue litmus to turn pink and (basic) alkaline if it causes red litmus to turn blue.



acid-base indicator a chemical substance that changes colour when the pH of the system changes

Figure 10 Lichen like this are used to make litmus.

Acid-Base Equilibrium 543

pH meter a device used to measure pH; based on the electric potential of a silver-silver chloride glass electrode and a saturated calomel (dimercury(I) chloride) electrode



Figure 11

A pH meter measures the voltage generated by a pH-dependent voltaic cell and the scale converts the millivolt reading into a pH reading.



Determining the pH of Common Substances (p. 626)

Most common household cleaning agents, foods, and beverages are acidic or basic solutions. Which methods are most suitable for measuring the pH of common household materials?

A **pH meter** is an electronic instrument that measures the voltage between electrodes in a solution and displays this measurement as a pH value (**Figure 11**).

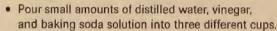
TRY THIS activity

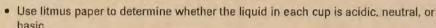
Magic Markers

Colour-changing markers have become a popular toy. The ink in these markers changes colour when drawn over with a special white "magic" marker, creating a stunning visual effect. Why does the coloured ink change colour when mixed with the substance in the white marker?

Materials: lab apron; set of colour-changing markers (including the "magic" marker); 3 small plastic cups; 3 cotton swabs; sheet of blank white paper; white vinegar (5% acetic acid); dilute baking soda solution; distilled water; red cabbage leaf

- Draw horizontal parallel lines on the sheet of white paper, using all of the different coloured markers. The lines should be at least 0.5 cm wide, 6 cm long, and 1 cm apart.
- Draw another horizontal line equally spaced from the first three using the cut edge of a folded red cabbage leaf.
- Using the "magic" marker, draw a single vertical line, perpendicular to the coloured lines, that crosses each of the coloured lines. Label this line "magic marker."





- Dip the tip of a cotton swab into the distilled water and draw a vertical line across all of the coloured lines, as you did earlier with the magic marker. Label this line "water." Also indicate whether the liquid is acidic, neutral, or basic.
- Using a new cotton swab each time, draw new vertical lines with vinegar and baking soda solution. Label these lines accordingly.
- · Record your observations in a suitable table.
 - (a) Provide a hypothesis to explain the effect of the "magic" marker on the coloured ink and cabbage juice mark.
 - (b) Describe a procedure to test your hypothesis. If possible, carry out the test.

The pH of Strong Acids

Strong acids ionize quantitatively in aqueous solution. As you already know, a 0.1 mol/L $HCl_{(aq)}$ solution has virtually no HCl molecules in it. We assume that it contains 0.1 mol/L $H^+_{(aq)}$ and 0.1 mol/L $Cl^-_{(aq)}$. The pH of this solution is 1.0, since the negative logarithm of 0.1 is 1. In general, the pH of solutions of strong monoprotic acids is calculated from the concentration of $H^+_{(aq)}$ ions, which is assumed to be equal to the molar concentration of the solute molecules (before ionization).

Calculating the pH, pOH, and $[OH_{fag}]$ of a Strong Acid

Calculate the pH, pOH, and $[OH_{(aq)}^-]$ of a 0.042 mol/L HNO_{3(aq)} solution (Figure 12).

This problem is similar to an earlier sample problem in which we calculated the [OH_{fact}] of a solution of a strong acid. In this case, we take the problem one step further and calculate the pH and pOH of the solution.

Appendix C7 lists HNO₃ as a strong acid. Therefore, we assume that it ionizes 100% when it dissolves in water at SATP:

$$HNO_{3(aq)} \xrightarrow{100\%} H_{(aq)}^+ + NO_{3(aq)}^-$$

The major entities in solution are $H_{(aq)}^+$, $NO_{3(aq)}^-$, and $H_2O_{(1)}$. In 0.04 mol/L HNO_{3(aq)},

$$[H_{(aq)}^+] = 0.040 \text{ mol/L}$$

We can ignore the miniscule contributions to [H_(aq)] made by the autoionization of water and the presence of NO3 (aq) (the weak conjugate base of HNO3).

First, calculate pH.

$$pH = -log[H_{(aq)}^+]$$

= $-log(0.040)$
 $pH = 1.40$

Then calculate pOH.

$$pH + pOH = 14.00$$

 $pOH = 14.00 - pH$
 $= 14.00 - 1.40$
 $pOH = 12.60$

Using the value of pOH, we can now calculate the concentration of hydroxide ions in the solution:

$$[OH^{-}_{(aq)}] = 10^{-pOH}$$

= $10^{-12.60} \text{ mol/L}$
 $[OH^{-}_{(aq)}] = 2.5 \times 10^{-13} \text{ mol/L}$

The pH of the solution is 1.40; the pOH is 12.60; and the $[OH_{(aq)}^-]$ is 2.5×10^{-13} mol/L.

Example

Calculate the pH, pOH, and $[OH_{(aq)}^-]$ of a 0.0020 mol/L $HBr_{(aq)}$ solution. (HBr is a strong acid used mostly in the halogenation of organic chemicals.)

Solution

$$HBr_{(1)} \xrightarrow{100\%} H^{+}_{(aq)} + Br^{-}_{(aq)}$$

The major entities are $H_{(aq)}^+$, $Br_{(aq)}^-$, and $H_2O_{(j)}$.

$$[H_{(aq)}^+] = 0.0020 \text{ mol/L}$$

We can ignore the small [H_[aq]] produced by the autoionization of water, and the presence of Br_(aq).

SAMPLE problem



Figure 12 Nitric acid is produced commercially using a process invented by Wilhelm Ostwald (1853-1932).

$$pH = -log [H_{(aq)}^+]$$

$$= -log(0.0020)$$

$$pH = 2.70$$

$$pOH = 14.0 - pH$$

$$= 14.0 - 2.7$$

$$pOH = 11.30$$

$$[OH_{(aq)}^-] = 10^{-pOH}$$

$$= 10^{-11.30} \text{ mol/L}$$

$$[OH_{(aq)}^-] = 5.0 \times 10^{-12} \text{ mol/L}$$

Answers

12. (a) pH = 2.2
 pOH = 11.8

$$[OH_{(aq)}^{-}] = 2 \times 10^{-12} \text{ mol/L}$$

(b) pH = 1.60
 pOH = 12.40

$$[OH^-_{(aq)}] = 4.0 \times 10^{-13} \text{ mol/L}$$

(c) pH = 2.00
pOH = 12.00
[OH
$$_{(aq)}^{-}$$
] = 1.0 \times 10 $^{-12}$ mol/L

13.
$$pH = 14.64$$

 $pOH = -0.64$

14.
$$m_{KOH} = 0.09 g$$

15. (a)
$$[OH_{(aq)}]_{oranges} = 1.8 \times 10^{-12} \text{ mol/L}$$

 $pH_{oranges} = 2.26$
 $pOH_{oranges} = 11.74$

$$[H_{(aq)}^{+}]_{asparagus} =$$

$$4 \times 10^{-9} \text{ mol/L}$$

$$[OH_{(aq)}^{-}]_{asparagus} =$$

$$3 \times 10^{-6} \text{ mol/L}$$

$$pH_{asparagus} = 8.4$$

$$[H_{(aq)}^+]_{olives} = 5.0 \times 10^{-4} \text{ mol/L}$$

$$pH_{olives} = 3.30$$

$$pOH_{olives} = 10.70$$

$$[H^{+}_{(aq)}]_{blackberries} = 4.0 \times 10^{-4} \text{ mol/L}$$

 $[OH^{-}_{(aq)}]_{blackberries} = 2.5 \times 10^{-11} \text{ mol/L}$
 $pH_{blackberries} = 3.40$

Practice

Understanding Concepts

- Calculate the pH, pOH, and [OH_(aq)] of each of the following solutions.
 - (a) 0.006 mol/L HI(aq)
 - (b) 0.025 mol/L HNO_{3(aq)}
 - (c) 0.010 mol/L HCl_(aq)
- 13. To clean a clogged drain, 26 g of sodium hydroxide is added to water to make 150 mL of solution. What are the pH and pOH values for the solution?
- 14. What mass of potassium hydroxide is contained in 500 mL of solution that has a pH of 11.5?

Making Connections

15. Food scientists and dietitians measure the pH of foods when they devise recipes and special diets. The juices of various fruits and vegetables are extracted. Various measurements related to their acidity are made and recorded in Table 2 below.

Table 2 Acidity of Foods

| Food | [H ⁺ _(aq)] (mol/L) | [OH _(aq)] (mol/L) | pH | рОН |
|--------------|---|-------------------------------|----|-------|
| oranges | 5.5×10^{-3} | | | |
| asparagus | | | | 5.6 |
| olives | | 2.0×10^{-11} | | |
| blackberries | | | | 10.60 |

- (a) Copy and complete Table 2.
- (b) Based on pH only, predict which of the foods would taste most sour, assuming that sour taste is directly proportional to pH.
- (c) Which of these foods might dietitians recommend to their patients to help relieve heartburn? Why?
- (d) There is some research that suggests that women's diets may affect the likelihood of their getting pregnant, as sperm are sensitive to pH. Research this topic, and make some diet suggestions for a woman who is trying to get pregnant.



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- 16. When food enters the stomach, it stimulates the production and secretion of hydrochloric acid for digestion, reducing the pH of the stomach contents from 4 to 2.
 - (a) Compare the [H_(aq)] before and after the change in pH.
 - (b) Conduct library or Internet research to find out how the stomach protects itself from the corrosive effects of this low pH level.



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The pH of Strong Bases

The pH and the conductivity of a Ba(OH)_{2(aq)} solution are found to be higher than those of an NaOH(aq) solution of equal concentration. The barium hydroxide solution is more basic because barium hydroxide dissociates to yield two hydroxide ions per formula unit.

As with strong acids, the pOH and pH of strong bases are determined entirely by the [OH-(aq)] contributed by the dissociation of the ionic hydroxide solute. The contribution made by the autoionization of water is so small, in comparison, as to be negligible. Also, we assume that the metal cation produced by the dissociation of a strong base has no effect on the pH of the solution. The pOH of a basic solution may be calculated from the solution's pH by applying the equation pH + pOH = 14.0. For example, if the measured pH of a basic solution is 10.2, then

$$pH + pOH = 14.0$$

 $pOH = 14.0 - 10.2$
 $pOH = 3.8$

Calculating the pH of a Strong Base

Calculate the pH of a 0.02 mol/L NaOH_(aq) solution (Figure 13).

As usual, begin by writing the dissociation equation

$$NaOH_{(aq)} \xrightarrow{100\%} Na_{(aq)}^+ + OH_{(aq)}^-$$

The major entities are Na_(aq), OH_(aq) and H₂O₍₁₎.

Since NaOH is a strong base, we assume that it dissociates completely in solution. Thus, the hydroxide ion concentration will equal the concentration of NaOH given (0.02 mol/L).

$$[OH_{(aq)}^{-}] = 0.02 \text{ mol/L}$$

We can ignore the very small [OH-[aq]] produced by the autoionization of water, and the presence of Na_(aq).

$$pOH = -log[OH_{(aq)}^{-}]$$
$$= -log(0.02)$$
$$pOH = 1.7$$

Finally, calculate pH.

$$pH + pOH = 14.00$$

 $pH = 14.00 - pOH$
 $= 14.00 - 1.7$
 $pH = 12.3$

The pH of the sodium hydroxide solution is 12.3.

2. Calculate the pH and pOH of a solution prepared by dissolving 4.3 g of $Ba(OH)_{2(s)}$ in water to form 1.5 L of solution.

This problem is similar to an earlier sample problem in which we calculated the $[H^+_{(a\alpha)}]$ of a Ba(OH)_{2(aq)} solution. In this case, we take the problem one step farther and calculate the pH and pOH of the solution.

SAMPLE problem



Figure 13 One of the many uses of sodium hydroxide is as a bleaching agent, to whiten wood pulp before it is made into paper or cardboard.

First, we use the balanced equation for the dissociation of $Ba(OH)_{2(s)}$ in water to identify the major entities in solution.

$$\mathsf{Ba}(\mathsf{OH})_{2(\mathsf{aq})} \overset{\mathsf{100\%}}{\longrightarrow} \; \mathsf{Ba}_{(\mathsf{aq})}^{2+} \; + \; 2 \, \mathsf{OH}_{(\mathsf{aq})}^{-}$$

The major entities are $\mathrm{Ba^{2}^{+}_{(aq)}}$, $\mathrm{OH^{-}_{(aq)}}$, and $\mathrm{H_{2}O_{(j)}}$. Now calculate the amount of $\mathrm{Ba(OH)_{2(aq)}}$ that dissociates in solution.

$$n_{\text{Ba(OH)}_2} = 4.3 \text{ g/} \times \frac{1 \text{ mol}}{171.3 \text{ g/}}$$

$$n_{\text{Ba(OH)}_2} = 2.5 \times 10^{-2} \,\text{mol}$$

Use this value to calculate the $[Ba(OH)_{2(aq)}]$.

$$[Ba(OH)_{2(aq)}] = \frac{2.5 \times 10^{-2} \text{ moL}}{1.5 \text{ l}}$$

$$[Ba(OH)_{2(aq)}] = 1.7 \times 10^{-2} \text{ mol/L}$$

Every mole of Ba(OH)_{2(aq)} that dissociates, forms two moles of OH_{[aq)}. Therefore,

$$[OH_{(aq)}^{-}] = 2(1.7 \times 10^{-2} \text{ mol/L})$$

$$[OH^{-}_{(aq)}] = 3.3 \times 10^{-2} \text{ mol/L}$$

We can ignore the very small $[OH^-_{(aq)}]$ produced by the autoionization of water, and the presence of $Ba^{2+}_{(aq)}$. Therefore we can use the $[OH^-_{(aq)}]$ from the dissociation of $Ba(OH)_2$ to calculate the pOH of the solution.

$$pOH = -log[OH_{(aq)}^{-}]$$

$$= -\log(3.3 \times 10^{-2})$$

$$pOH = 1.47$$

Finally, calculate the pH.

$$pH + pOH = 14.00$$

$$pH = 14.00 - pOH$$

$$= 14.00 - 1.47$$

$$pH = 12.53$$

The pH of the solution is 12.53, and the pOH is 1.47.



Figure 14

Effluent at a sewage treatment plant tends to be acidic. The sewage can be neutralized by adding calcium hydroxide, also known as hydrated lime. In this automated plant, workers can control pH from terminals.

Example

Calculate the pH of a 0.002 mol/L $Ca(OH)_{2(aq)}$ solution (Figure 14).

Solution

$$Ca(OH)_{2(aq)} \longrightarrow Ca^{2+}_{(aq)} + 2OH^{-}_{(aq)}$$

The major entities are $Ca^{2+}_{(aq)}$, $OH^-_{(aq)}$, and $H_2O_{(aq)}$. In 0.002 mol/L $Ca(OH)_{2(aq)}$,

$$[OH_{(aq)}^{-}] = 2(0.002 \text{ mol/L})$$

$$[OH_{(aq)}^{-}] = 0.004 \text{ mol/L}$$

Ignore the very small [OH_[aq]] produced by the autoionization of water, and the presence of Ca(2+)

$$\begin{aligned} \text{pOH} &= -\text{log}[\text{OH}^-_{(aq)}] \\ &= -\text{log}(0.004) \\ \text{pOH} &= 2.4 \\ \\ \text{pH} &+ \text{pOH} &= 14.00 \\ \\ \text{pH} &= 14.00 - \text{pOH} \\ \\ &= 14.00 - 2.4 \end{aligned}$$

pH = 11.6

The pH of the calcium hydroxide solution is 11.6.

Practice

Understanding Basic Concepts

- 17. Calculate the pH of a 0.15 mol/L sodium hydroxide solution.
- 18. Calculate the pH of a 0.032 mol/L Ba(OH)_{2(aq)} solution.
- 19. A solution is made by dissolving 0.80 g Ca(OH)_{2(s)} in water to make 100 mL of final solution. Calculate the pH of the solution.

Answers

17. 13.18

18. 12.81

19. 13.33

SUMMARY

Summary pH and pOH

$$\begin{array}{rcl} {\cal K}_{W} &=& [H^{+}_{(aq)}][OH^{-}_{(aq)}] \\ & & p{\cal K}_{W} &=& -log{\cal K}_{W} \\ & pH &=& -log[H^{+}_{(aq)}] & pOH &=& -log[OH^{-}_{(aq)}] \\ & [H^{+}_{(aq)}] &=& 10^{-pH} & [OH^{-}_{(aq)}] &=& 10^{-pOH} \\ pH &+& pOH &=& 14.00 & (at SATP) \end{array}$$

Section 8.1 Questions

Understanding Concepts

- 1. How does the hydrogen ion concentration compare with the hydroxide ion concentration if a solution is
 - (a) neutral?
 - (b) acidic?
 - (c) basic?
- 2. What two diagnostic tests can distinguish a weak acid from a strong acid?
- 3. According to Arrhenius's theory, what do all bases have in common?
- 4. Calculate the mass of sodium hydroxide that must be dissolved to make 2.00 L of a solution with a pH of 10.35, at
- 5. According to the table of acid-base indicators (Appendix C10), what is the colour of each of the following indicators in the solutions of given pH?
 - (a) Litmus in a solution with a pH of 8.2
 - (b) Methyl orange in a solution with a pH of 3.9
- 6. Complete the analysis for each of the following diagnostic tests. If [the specified indicator] is added to a solution, and the colour of the solution turns [the given colour], then the solution pH is _

- (a) methyl red; red
- (b) alizarin yellow; red
- (c) bromocresol green; blue
- (d) bromothymol blue; green
- Separate samples of an unknown solution turned both methyl orange and bromothymol blue to yellow, and turned bromocresol green to blue.
 - (a) Estimate the pH of the unknown solution.
 - (b) Calculate the approximate hydrogen ion concentration.

Applying Inquiry Skills

8. Create an experimental design, using a flow chart or a table, that will identify each of four colourless solutions as one of: a strong acid solution; a weak acid solution; a neutral molecular solution; a neutral ionic solution.

Making Connections

 Conduct library or Internet research to obtain information to answer the following questions about gastroesophageal reflux disease, GERD.

- (a) What is GERD?
- (b) Who is usually affected by this condition?
- (c) Describe the apparatus used to diagnose this condition.
- (d) What treatments are currently available for this disease? Include examples of chemotherapeutic and surgical interventions.



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- Conduct library or Internet research to answer the following questions regarding acid-free paper.
 - (a) What is acid-free paper? Why is it called "acid-free"?
 - (b) What are the primary uses of acid-free paper?
 - (c) List advantages and disadvantages of its use.

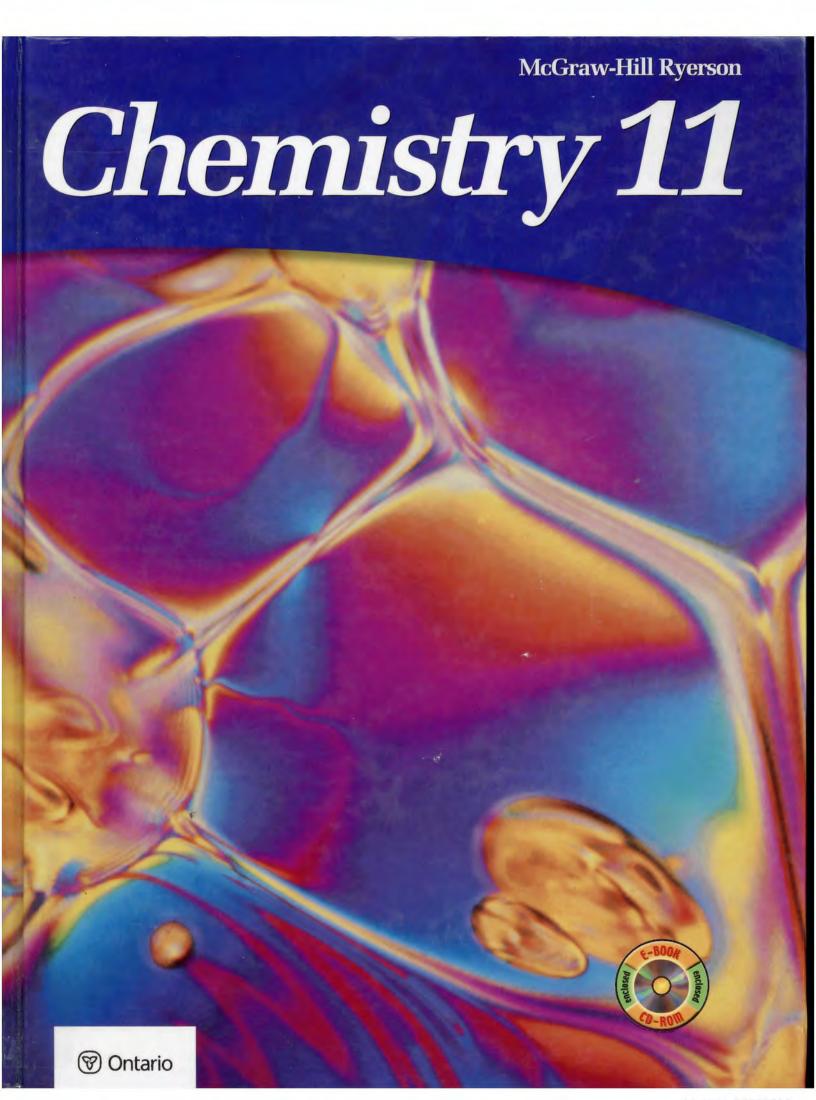


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EXHIBIT C

Previously Filed as ECF No. 63, Exhibit 7



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Chemistry 11

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0-07-088681-4

E-BOOK CD-ROM ISBN

0-07-089356-X

McGraw-Hill Ryerson Chemistry 11

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0-07-088681-4

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234567890 TRI 0987654321

Printed and bound in Canada

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National Library of Canada Cataloguing in Publication Data

Main entry under title:

McGraw-Hill Ryerson chemistry 11

Includes index.

ISBN 0-07-088681-4

1. Chemisty, I. Clancy, Christina. II. Title: Chemistry 11. III. Title: McGraw-Hill Ryerson chemistry eleven.

QD33. M33 2001 540 C2001-930333-5

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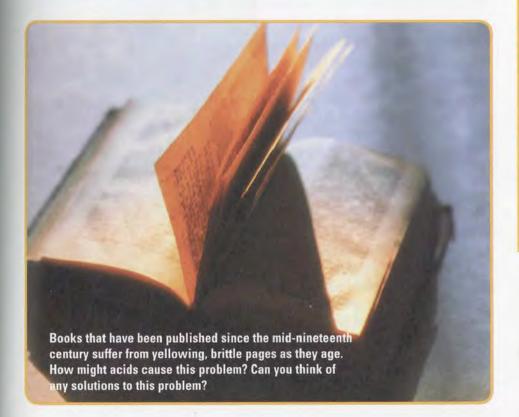
Acids and Bases

What do cheese, stomach juices, baking soda, oven cleaner, and underarm odour have in common? They are all acidic or basic. Do you know which are acidic and which are basic?

Acids and bases are very important chemicals. They have been used for thousands of years. Vinegar is an acidic solution that is common in many food and cleaning products. It was discovered long ago—before people invented the skill of writing to record its use. Today, acids are also used to manufacture fertilizers, explosives, plastics, motor vehicles, and computer circuit boards.

Like acids, bases have numerous uses in the home and in chemical industries. Nearly 5000 years ago, in the Middle East, the Babylonians made soap using the bases in wood ash. Today, one of Canada's most important industries, the pulp and paper industry, uses huge quantities of a base called sodium hydroxide. Sodium hydroxide is also used to manufacture soaps, detergents, dyes, and many other compounds.

In this chapter, you will learn about the properties of acids and bases. You will learn how these properties change when acids and bases react together. As well, you will have a chance to estimate and measure the acidity of aqueous solutions.



Chapter Preview

- 10.1 Acid-Base Theories
- 10.2 Strong and Weak Acids and Bases
- 10.3 Acid-Base Reactions

Concepts and Skills You Will Need

Before you begin this chapter, review the following concepts and skills:

- describing and calculating the concentration of solutions (Chapter 8, section 8.2)
- performing stoichiometry calculations (Chapter 7, section 7.2)
- naming and identifying polyatomic ions and their formulas (Chapter 3, section 3.4)

10.1

Acid-Base Theories

Section Preview/ Specific Expectations

In this section, you will

- describe and compare the Arrhenius and Brønsted-Lowry theories of acids and
- identify conjugate acid-base pairs
- communicate your understanding of the following terms: Arrhenius theory of acids and bases, hydronium ion, Brønsted-Lowry theory of acids and bases, conjugate acid-base pair, conjugate base, conjugate acid

As you can see in Table 10.1, acids and bases are common products in the home. It is easy to identify some products as acids. Often the word "acid" appears in the list of ingredients. Identifying bases is more difficult. Acids and bases have different properties, however, that enable you to distinguish between them.

Table 10.1 Common Acids and Bases in the Home

| | cids | |
|--|--|--|
| Product | Acid(s) contained in the product | |
| citrus fruits (such as lemons, limes, oranges and tomatoes) | citric acid and ascorbic acid | |
| dairy products (such as cheese, milk, and yogurt) | lactic acid | |
| vinegar | acetic acid | |
| soft drinks | carbonic acid; may also contain phosphoric acid and citric acid | |
| underarm odour | 3-methyl-2-hexenoic acid | |
| | ases | |
| Product | Base contained in the product | |
| oven cleaner | sodium hydroxide | |
| baking soda | sodium hydrogen carbonate | |
| washing soda | sodium carbonate | |
| glass cleaner (some brands) | ammonia | |

Language

LINK

The word "acid" comes from the Latin acidus, meaning "sour tasting." As you will learn in this chapter, bases are the "base" (the foundation) from which many other compounds form. A base that is soluble in water is called an alkali. The word "alkali" comes from an Arabic word meaning "ashes of a plant." In the ancient Middle East, people rinsed plant ashes with hot water to obtain a basic solution. The basic solution was then reacted with animal fats to make soap.

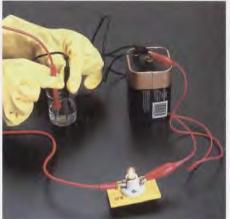
Properties of Acids and Bases

One way to distinguish acids from bases is to describe their observable properties. For example, acids taste sour, and they change colour when mixed with coloured dyes called indicators. Bases taste bitter and feel slippery. They also change colour when mixed with indicators.

CAUTION You should never taste or touch acids, bases, or any other chemicals. Early chemists used their senses of taste and touch to observe the properties of many chemicals. This dangerous practice often led to serious injury, and sometimes death.

Another property that can be used to distinguish acids from bases is their conductivity in solution. As you can see in Figure 10.1, aqueous solutions of acids and bases conduct electricity. This is evidence that ions are present in acidic and basic solutions. Some of these solutions, such as hydrochloric acid and sodium hydroxide (a base), cause the bulb to glow brightly. Most acidic and basic solutions, however, cause the bulb to glow dimly.





hydrochloric acid, HCI(aq) (1 mol/L)





acetic acid, CH₃COOH_(aq) (1 mol/L)

sodium hydroxide, NaOH(aq) (1 mol/L)



Figure 10.1 Aqueous solutions of acids and bases can be tested using a conductivity tester. The brightness of the bulb is a clue to the concentration of ions in the solution. Which of these solutions have higher concentrations of ions? Which have lower concentrations?

Table 10.2 on the next page summarizes the observable properties of acids and bases. These observable properties include their physical characteristics and their chemical behaviour. The Express Lab on page 373 provides you with an opportunity to compare some of these properties. What are acids and bases, however? How does chemical composition determine whether a substance is acidic or basic? You will consider one possible answer to this question starting on page 373.

An oxide is a compound of oxygen with a metal or non-metal. Most metal oxides react with water to form basic solutions. For example, calcium oxide is a metal oxide that is important in the construction industry as an ingredient of cement. Calcium oxide reacts with water to form a basic solution of calcium hydroxide.

 $CaO_{(s)} + H_2O_{(\ell)} \rightarrow Ca(OH)_{2(aq)}$ Many municipal water treatment plants use calcium hydroxide to soften very hard water before releasing it for public use. Most non-metal oxides react with water to form acidic solutions. For example, sulfur dioxide gas dissolves in water to form sulfurous acid.

 $SO_{2(q)} + H_2O_{(\ell)} \rightarrow H_2SO_{3(aq)}$ The metallic character of the elements in the periodic table, and the acid-base properties of their oxides, show a distinct trend across periods and down groups. Infer what this trend is. In other words, state what you think happens to the acid-base properties of oxides as you go across a period and down a group. Make a quick sketch of the periodic table to illustrate this trend. How would you describe the acid-base properties of the metalloids? (Use your knowledge of the physical properties of the metalloids to help you make your inference.)

Table 10.2 Some Observable Properties of Acids and Bases

| Property | | | |
|--------------|-------------------------------------|--------------------------------|--|
| Taste | Electrical conductivity in solution | Feel of solution | |
| taste sour | conduct electricity | have no characteristic feel | |
| taste bitter | conduct electricity | feel slippery | |
| Tonics | | | |

Property Reaction with Reaction with Reaction with active metals litmus paper carbonate compounds Acids turns blue produce carbon produce litmus red hydrogen gas dioxide gas Bases turn red do not react do not react litmus blue

ACIDS

ACIDS

BASES

BASES

ExpressLab



Clean a Penny

Many cleaning products contain an acid or a base. For example, some window cleaners contain vinegar (acetic acid). Other window cleaners contain ammonia (a base). Oven cleaners, however, contain only bases. This activity will help you infer why.

Safety Precautions







Materials

water vinegar 100 mL graduated cylinder spoon or scoopula baking soda 3 small beakers (about 200 mL) 3 tarnished pennies

Procedure

- 1. Predict which solution(s) will clean the penny best. Give reasons for your prediction.
- 2. In one beaker, mix 50 mL of vinegar with about 150 mL of water. In a second beaker,

- mix about 20 mL to 30 mL spoonfuls of baking soda with 150 mL of water. In the third beaker, put only 150 mL of water.
- 3. Place a tarnished penny in each beaker. Observe what happens for about 15 min.

Analysis

- 1. Which solution was the best cleaner? How did your observations compare with your prediction?
- 2. What results would you expect if you tried cleaning a penny in a solution of lemon juice? What if you used a dilute solution of ammonia? Note: If you want to test your predictions, ask your teacher for the concentrations of the solutions you should use.
- 3. The base that is often used in oven cleaners is sodium hydroxide. This base is very corrosive, and it can burn skin easily. A corrosive acid, such as hydrochloric acid, could also remove baked-on grease and grime from ovens. Why are bases a better choice for oven cleaners?

The Arrhenius Theory of Acids and Bases

In Figure 10.1, you saw evidence that ions are present in solutions of acids and bases. When hydrogen chloride dissolves in water, for example, it dissociates (breaks apart) into hydrogen ions and chloride ions.

$$HCl_{(aq)} \rightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$$

When sodium hydroxide dissolves in water, it dissociates to form sodium ions and hydroxide ions.

$$NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$$

The dissociations of other acids and bases in water reveal a pattern. This pattern was first noticed in the late nineteenth century hy a Swedish chemist named Svanté Arrhenius. (See Figure 10.2.)

$$HBr_{(aq)} \rightarrow H^{+}_{(aq)} + Br_{(aq)}^{-}$$

$$H_2SO_{4(aq)} \rightarrow H^+_{(aq)} + HSO^-_{4(aq)}$$

$$HClO_{4(aq)} \rightarrow \mathbf{H}^{+}_{(aq)} + ClO^{-}_{4(aq)}$$

$$LiOH_{(aq)} \rightarrow Li^{+}_{(aq)} + OH^{-}_{(aq)}$$

$$KOH_{(aq)} \rightarrow K^{+}_{(aq)} + OH^{-}_{(aq)}$$

$$Ba(OH)_{2(aq)} \rightarrow Ba^{+}_{(aq)} + 2OH^{-}_{(aq)}$$

acids dissociating in water, and their resulting ions

bases dissociating in water, and their resulting ions



Figure 10.2 Svanté Arrhenius (1859 - 1927).



www.school.mcgrawhill.ca/

Scientists did not embrace the Arrhenius theory when they first heard about it during the 1880s. Why were they unimpressed with this theory? What was necessary to convince them? Arrhenius is featured on several web sites on the Internet. To link with these web sites, go to the web site above. Go to Science Resources, then to Chemistry 11 to find out where to go next.

In 1887, Arrhenius published a theory to explain the nature of acids and bases. It is called the Arrhenius theory of acids and bases.

The Arrhenius Theory of Acids and Bases

- · An acid is a substance that dissociates in water to produce one or more hydrogen ions, H+.
- · A base is a substance that dissociates in water to form one or more hydroxide ions, OH.

According to the Arrhenius theory, acids increase the concentration of H+ in aqueous solutions. Thus, an Arrhenius acid must contain hydrogen as the source of H+. You can see this in the dissociation reactions for acids on the previous page.

Bases, on the other hand, increase the concentration of OH in aqueous solutions. An Arrhenius base must contain the hydroxyl group, —OH. as the source of OH-. You can see this in the dissociation reactions for bases on the previous page.

Limitations of the Arrhenius Theory

The Arrhenius theory is useful if you are interested in the ions that result when an acid or a base dissociates in water. It also helps explain what happens when an acid and a base undergo a neutralization reaction. In such a reaction, an acid combines with a base to form an ionic compound and water. Examine the following reactions:

$$HCI_{(aq)} + NaOH_{(aq)} \rightarrow NaCI_{(aq)} + H_2O_{(\ell)}$$

The net ionic equation for this reaction shows the principal ions in the Arrhenius theory.

$$H^{+}_{(aq)} + OH^{-}_{(aq)} \rightarrow H_{2}O_{(\ell)}$$

Since acids and bases produce hydrogen ions and hydroxide ions, water is an inevitable result of acid-base reactions.

Problems arise with the Arrhenius theory, however. One problem involves the ion that is responsible for acidity: H+. Look again at the equation for the dissociation of hydrochloric acid.

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

This dissociation occurs in aqueous solution, but chemists often leave out H₂O as a component of the reaction. They simply assume that it is there. What happens if you put H_2O into the equation?

$$HCl_{(aq)} + H_2O_{(\ell)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(\ell)}$$

Notice that the water is unchanged when the reaction is represented this way. However, you learned earlier that water is a polar molecule. The O atom has a partial negative charge, and the H atoms have partial positive charges. Thus, H2O must interact in some way with the ions H+ and Cl-. In fact, chemists made a discovery in the early twentieth century. They realized that protons do not exist in isolation in aqueous solution. (The hydrogen ion is simply a proton. It is a positively charged nuclear particle.) Instead, protons are always hydrated: they are attached to water molecules. A hydrated proton is called a hydronium ion, H₃O⁺(aq). (See Figure 10.3.)

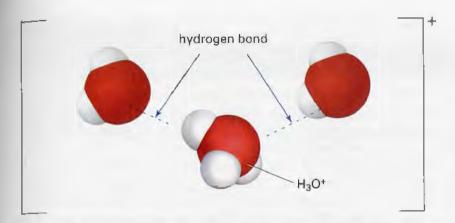


Figure 10.3 For convenience, chemists often use H+(ag) as a shorthand notation for the hydronium ion, H₃O+(ac). Hydronium ions do not exist molecules. Thus, a more correct formula is $H^+(H_2O)_n$, where n is usually 4 or 5.

There is another problem with the Arrhenius theory. Consider the reaction of ammonia, NH3, with water.

$$NH_{3(g)} + H_2O_{(t)} \rightarrow NH^+_{4(aq)} + OH^-_{(aq)}$$

Ammonia is one of several substances that produce basic solutions in water. As you can see, ammonia does not contain hydroxide ions. However, it does produce these ions when it reacts with water. Ammonia also undergoes a neutralization reaction with acids. The Arrhenius theory cannot explain the basic properties of ammonia. Nor can it explain the fact that certain other substances, such as salts that contain carbonate ions, also have basic properties.

There is yet another problem with the Arrhenius theory. It is limited to acid-base reactions in a single solvent, water. Many acid-base reactions take place in other solvents, however.

The Brønsted-Lowry Theory of Acids and Bases

In 1923, two chemists working independently of each other, proposed a new theory of acids and bases. (See Figure 10.4.) Johannes Brønsted in Copenhagen, Denmark, and Thomas Lowry in London, England, proposed what is called the Brønsted-Lowry theory of acids and bases. This theory overcame the problems related to the Arrhenius theory.

The Brønsted-Lowry Theory of Acids and Bases

- An acid is a substance from which a proton (H⁺ ion) can be removed.
- · A base is a substance that can remove a proton (H+ ion) from an acid.





independently. Instead, they form hydrogen bonds with other water

CHECKPOINT

Use the idea of the hydronium ion to complete the following equation:

 $HCI_{(aq)} + H_2O_{(\ell)} \rightarrow$

Figure 10.4 Johannes Brønsted (1879-1947), left, and Thomas Lowry (1874-1936), right. Brønsted published many more articles about ions in solution than Lowry did. Thus, some chemistry resources refer to the "Brønsted theory of acids and bases."



In many chemistry references, Brønsted-Lowry acids are called "proton donors." Brønsted-Lowry bases are called "proton acceptors." Although these terms are common, they create a false impression about the energy that is involved in acid-base reactions. Breaking bonds always requires energy. For example, removing a proton from a hydrochloric acid molecule requires 1.4×10^3 kJ/mol. This is far more energy than the word "donor" implies.

Like an Arrhenius acid, a Brønsted-Lowry acid must contain H in its formula. This means that all Arrhenius acids are also Brønsted-Lowry acids. However, any negative ion (not just OH-) can be a Brønsted-Lowry base. In addition, water is not the only solvent that can be used.

According to the Brønsted-Lowry theory, there is only one requirement for an acid-base reaction. One substance must provide a proton, and another substance must receive the same proton. In other words, an acidbase reaction involves the transfer of a proton.

The idea of proton transfer has major implications for understanding the nature of acids and bases. According to the Brønsted-Lowry theory. any substance can behave as an acid, but only if another substance behaves as a base at the same time. Similarly, any substance can behave as a base, but only if another substance behaves as an acid at the same time.

For example, consider the reaction between hydrochloric acid and water shown in Figure 10.5. In this reaction, hydrochloric acid is an acid because it provides a proton (H+) to the water. The water molecule receives the proton. Therefore, according to the Brønsted-Lowry theory, water is a base in this reaction. When the water receives the proton, it becomes a hydronium ion (H₃O⁺). Notice the hydronium ion on the right side of the equation.

proton transfer conjugate acid
$$HCl_{\{aq\}} + H_2O_{\{\ell\}} \rightarrow H_3O^+_{\{aq\}} + Cl^-_{\{aq\}}$$
 acid base conjugate base

Figure 10.5 The reaction between hydrochloric acid and water, according to the Brønsted-Lowry theory

Two molecules or ions that are related by the transfer of a proton are called a conjugate acid-base pair. (Conjugate means "linked together.") The conjugate base of an acid is the particle that remains when a proton is removed from the acid. The conjugate acid of a base is the particle that results when the base receives the proton from the acid. In the reaction between hydrochloric acid and water, the hydronium ion is the conjugate acid of the base, water. The chloride ion is the conjugate base of the acid. hydrochloric acid.

According to the Brønsted-Lowry theory, every acid has a conjugate base, and every base has a conjugate acid. The conjugate base and conjugate acid of an acid-base pair are linked by the transfer of a proton. The conjugate base of the acid-base pair has one less hydrogen than the acid. It also has one more negative charge than the acid. The conjugate acid of the acid-base pair has one more hydrogen than the base. It also has one less negative charge than the base.

These ideas about acid-base reactions and conjugate acid-base pairs will become clearer as you study the following Sample Problems and Practice Problems.

Sample Problem

Conjugate Acid-Base Pairs

Problem

Hydrogen bromide is a gas at room temperature. It is soluble in water, forming hydrobromic acid. Identify the conjugate acid-base pairs.

What Is Required?

You need to identify two sets of conjugate acid-base pairs.

What Is Given?

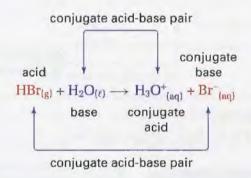
You know that hydrogen bromide forms hydrobromic acid in aqueous solution.

Plan Your Strategy

- · Write a balanced chemical equation.
- · On the left side of the equation, identify the acid as the molecule that provides the proton. Identify the base as the molecule that accepts the proton.
- On the right side of the equation, identify the particle that has one proton less than the acid on the left side as the conjugate base of the acid. Identify the particle on the right side that has one proton more than the base on the left side as the conjugate acid of the base.

Act on Your Strategy

Hydrogen bromide provides the proton, so it is the Brønsted-Lowry acid in the reaction. Water receives the proton, so it is the Brønsted-Lowry base. The conjugate acid-base pairs are HBr/Br and H2O/H3O+.



Check Your Solution

The formulas of the conjugate pairs differ by one proton, H+, as expected.

Sample Problem

More Conjugate Acid-Base Pairs

Problem

Ammonia is a pungent gas at room temperature. Its main use is in the production of fertilizers and explosives. It is very soluble in water. It forms a basic solution that is used in common products, such as glass cleaners. Identify the conjugate acid-base pairs in the reaction between aqueous ammonia and water.

$$NH_{3(g)} + H_2O_{(\ell)} \rightarrow NH_4^{+}_{(aq)} + OH^{-}_{(aq)}$$

What Is Required?

You need to identify the conjugate acid-base pairs.

What Is Given?

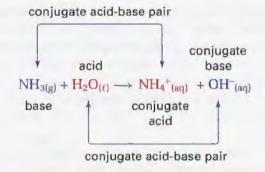
The chemical equation is given.

Plan Your Strategy

- · Identify the proton-provider on the left side of the equation as the acid. Identify the proton-remover (or proton-receiver) as the base.
- · Identify the conjugate acid and base on the right side of the equation by the difference of a single proton from the acid and base on the left side.

Act on Your Strategy

The conjugate acid base pairs are NH₄+/NH₃ and H₂O/OH-.



Check Your Solution

The formulas of the conjugate pairs differ by a proton, as expected.

Practice Problems

1. Hydrogen cyanide is a poisonous gas at room temperature. When this gas dissolved in water, the following reaction occurs:

$$HCN_{(aq)} + H_2O_{(\ell)} \rightarrow H_3O^+_{(aq)} + CN^-_{(aq)}$$

Identify the conjugate acid-base pairs.

Continued

PROBLEM TIP

In the previous Sample Problem, water acted as a base. In this Sample Problem, water acts as an acid.

Remember: Water can act as a proton-provider (an acid) in some reactions and as a proton-receiver (a base) in others.



2. Sodium acetate is a good electrolyte. In water, the acetate ion reacts as follows:

$$CH_3COO^-_{(aq)} + H_2O_{(\ell)} \rightarrow CH_3COOH_{(aq)} + OH^-_{(aq)}$$
 Identify the conjugate acid-base pairs.

3. Write equations to show how the hydrogen sulfide ion, HS⁻, can react with water. First show the ion acting as an acid. Then show the ion acting as a base.

Section Wrap-up

The two theories that you have considered in this section attempt to explain the chemical nature of acids and bases. Table 10.3 summarizes the key points of these theories.

In both the Arrhenius theory and the Brønsted-Lowry theory, acids and bases form ions in solution. Many characteristics of acid-base behaviour are linked to the number of ions that form from a particular acid or base. One of these characteristics is strength.

In section 10.2, you will learn why a dilute solution of vinegar is safe to ingest, while the same molar concentration of hydrochloric acid would be extremely poisonous.

Table 10.3 Comparing the Arrhenius Theory and the Bronsted-Lowry Theory

| Theory | Arrhenius | Brenstead-Lowry |
|---------|--|---|
| Acid | any substance that dissociatesto form H ⁺ in aqueous solution | any substance that provides a proton to another substance (or any substance from which a proton may be removed) |
| Base | any substance that dissociates to form OH ⁻ in aqueous solution | any substance that receives a proton from an acid (or any substance that removes a proton from an acid) |
| Example | $HCl_{(aq)} \rightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$ | $HCl_{(aq)} + H_2O_{(\ell)} \rightarrow H_3O^+_{(aq)} + Cl^{(aq)}$ |

Section Review

O Suppose that you have four unknown solutions, labelled A, B, C, and D. You use a conductivity apparatus to test their conductivity, and obtain the results shown below. Use these results to answer the questions that follow.

| Solution | Results of Conductivity Test | |
|----------|-------------------------------------|--|
| A | the bulb glows dimly | |
| В | the bulb glows strongly | |
| C | the bulb does not glow | |
| D | the bulb glows strongly | |

- (a) Which of these solutions has a high concentration of dissolved ions? What is your evidence?
- (b) Which of these solutions has a low concentration of dissolved ions? What is your evidence?

- (c) Which of the four unknowns are probably aqueous solutions of acids or bases?
- (d) Based on these tests alone, can you distinguish the acidic solution(s) from the basic solutions(s)? Why or why not?
- (e) Suggest one way that you could distinguish the acidic solution(s) from the basic solution(s).
- 2 (a) WD Define an acid and a base according to the Arrhenius theory.
 - (b) Give two examples of observations that the Arrhenius theory can explain.
 - (c) Give two examples of observations that the Arrhenius theory can not explain.
- (a) (Define an acid and a base according to the Brønsted-Lowry
 - (b) What does the Brønsted-Lowry theory have in common with the Arrhenius theory? In what ways is it different?
 - (c) Which of the two acid-base theories is more comprehensive? (In other words, which explains a broader body of observations?)
- (a) What is the conjugate acid of a base?
 - (b) What is the conjugate base of an acid?
 - (c) Use an example to illustrate your answers to parts (a) and (b) above.
- Write the formula for the conjugate acid of the following:
 - (a) the hydroxide ion, OH-
 - (b) the carbonate ion, CO32-
- 6 WD Write the formula for the conjugate base of the following: (a) nitric acid, HNO3
 - (b) the hydrogen sulfate ion, HSO4
- Which of the following compounds is an acid according to the Arrhenius theory?
 - (a) H₂O
 - (b) Ca(OH)2
 - (c) H₃PO₃
 - (d) HF
- Which of the following compounds is a base according to the Arrhenius theory?
 - (a) KOH
 - (b) Ba(OH)2
 - (c) HClO
 - (d) H₃PO₄
- Hydrofluoric acid dissociates in water to form fluoride ions.
 - (a) Write a balanced chemical equation for this reaction.
 - (b) Identify the conjugate acid-base pairs.
 - (c) Explain how you know whether or not you have correctly identified the conjugate acid-base pairs.
- 10 I dentify the conjugate acid-base pairs in the following reactions:
 - (a), $H_2PO_4^{-}_{(aq)} + CO^{2-}_{3(aq)} \rightarrow HPO_4^{2-}_{(aq)} + HCO_3^{-}_{(aq)}$
 - (b) $HCOOH_{(aq)} + CN^{-}_{(aq)} \rightarrow HCOO^{-}_{(aq)} + HCN_{(aq)}$
 - (c) $H_2PO_4^{-}(aq) + OH^{-}(aq) \rightarrow HPO_4^{2-}(aq) + H_2O_{(\ell)}$

Strong and Weak Acids and Bases

10.2

Re-examine Figure 10.1 on page 371. Look at the photographs of hydrochloric acid and acetic acid. The conductivity tester is testing the same concentrations of both acids. As you can see, the bulb glows brightly in the hydrochloric acid. The bulb glows dimly in the acetic acid. How can these different results be explained?

Strong Acids and Weak Acids

You know that ions are present in an aqueous solution of an acid. These ions result from the dissociation of the acid. An acid that dissociates completely into ions in water is called a strong acid. For example, hydrochloric acid is a strong acid. All the molecules of hydrochloric acid in an aqueous solution dissociate into H+ and Cl- ions. The H+ ions, as you know, bond with surrounding water molecules to form hydronium ions, H₃O+. (See Figure 10.6.) The concentration of hydronium ions in a dilute solution of a strong acid is equal to the concentration of the acid. Thus, a 1.0 mol/L solution of hydrochloric acid contains 1.0 mol/L of hydronium ions. Table 10.4 lists the strong acids.

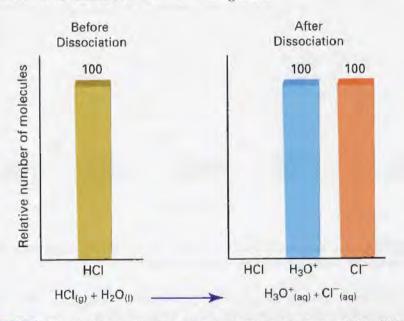


Figure 10.6 When hydrogen chloride molecules enter an aqueous solution, 100% of the hydrogen chloride molecules dissociate. As a result, the solution contains the same percent of H+ ions (in the form of H₃O+) and Cl- ions: 100%.

A weak acid is an acid that dissociates very slightly in a water solution. Thus, only a small percentage of the acid molecules break apart into ions. Most of the acid molecules remain intact. For example, acetic acid is a weak acid. On average, only about 1% (one in a hundred) of the acetic acid molecules dissociate at any given moment in a 0.1 mol/L solution. (The number of acid molecules that dissociate depends on the concentration and temperature of the solution.) In fact, the concentration of hydronium ions in a solution of a weak acid is always less than the concentration of the dissolved acid. (See Figure 10.7.)

Section Preview/ Specific Expectations

In this section, you will

- explain, in terms of the degree to which they dissociate, the difference between strong and weak acids and bases
- distinguish between binary acids and oxoacids
- define pH, and experimentally determine the effect on pH of diluting an acidic solution
- communicate your understanding of the following terms: strong acid, weak acid, strong base, weak base, binary acid, oxoacid, pH

Table 10.4 Strong Acids

| hydrochloric acid, HCl | |
|---|--|
| hydrobromic acid, HBr | |
| hydroiodic acid, HI | |
| nitric acid, HNO ₃ | |
| sulfuric acid, H ₂ SO ₄ | |
| perchloric acid, HClO ₄ | |
| | |

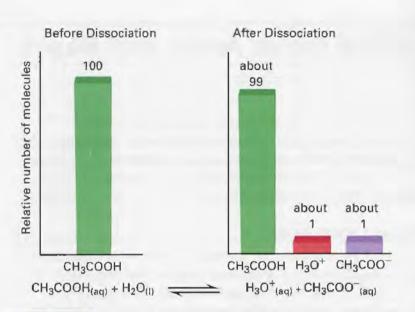


Figure 10.7 When acetic acid molecules enter an aqueous solution, only about 1% of them dissociate. Thus, the number of acetic acid molecules in solution is far greater than the number of hydronium ions and acetate ions.

Notice the arrow that is used in the equation in Figure 10.7. It points in both directions, indicating that the reaction is reversible. In other words, the products of the reaction also react to produce the original reactants. In this reaction, molecules of acetic acid dissociate just as quickly and as often as the dissociated ions re-associate to produce acetic acid molecules. (Figure 10.8 will help you visualize what happens.)

Most acids are weak acids. Whenever you see a reversible chemical equation involving an acid, you can safely assume that the acid is weak.



Figure 10.8 When acetic acid dissolves in water, acetic acid molecules dissociate and re-associate at the same time and at the same rate.

A few acids contain only a single hydrogen ion that can dissociate. These acids are called monoprotic acids. (The prefix mono- means "one." The root -protic refers to "proton.") Hydrochloric acid, hydrobromic acid. and hydroiodic acid are strong monoprotic acids. Hydrofluoric acid, HF, is weak monoprotic acid.

Many acids contain two or more hydrogen ions that can dissociate. For example, sulfuric acid, H2SO4(aq), has two hydrogen ions that can dissociate. As you know from Table 10.4, sulfuric acid is a strong acid. This is true only for its first dissociation, however.

$$H_2SO_{4(aq)} \rightarrow H^+_{(aq)} + HSO_4^-_{(aq)}$$

The resulting aqueous hydrogen sulfate ion, HSO-4, is a weak acid. It dissociates to form the sulfate ion in the following reversible reaction:

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

Thus, acids that contain two hydrogen ions dissociate to form two anions. These acids are sometimes called diprotic acids. (The prefix di-, as you know, means "two.") The acid that is formed by the first dissociation is stronger than the acid that is formed by the second dissociation.

Acids that contain three hydrogen ions are called triprotic acids. Phosphoric acid, H₃PO_{4(aq)}, is a triprotic acid. It gives rise to three anions, as follows:

$$H_3PO_{4(aq)} + H_2O_{(\ell)} \Rightarrow H^+_{(aq)} + H_2PO_{4^-_{(aq)}}$$

 $H_2PO_{4^-_{(aq)}} + H_2O_{(\ell)} \Rightarrow H^+_{(aq)} + HPO_{4^{2^-_{(aq)}}}$
 $HPO_{4^{2^-_{(aq)}}} + H_2O_{(\ell)} \Rightarrow H^+_{(aq)} + PO_{4^{3^-_{(aq)}}}$

Here again, the acid that is formed by the first dissociation is stronger than the acid that is formed by the second dissociation. This acid is stronger than the acid that is formed by the third dissociation. Keep in mind, however, that all three of these acids are weak because only a small proportion of them dissociates.

Strong Bases and Weak Bases

Like a strong acid, a strong base dissociates completely into ions in water. All oxides and hydroxides of the alkali metals—Group 1 (IA)—are strong bases. The oxides and hydroxides of the alkaline earth metals—Group 2 (IIA)—below beryllium are also strong bases.

Recall that the concentration of hydronium ions in a dilute solution of a strong acid is equal to the concentration of the acid. Similarly, the concentration of hydroxide ions in a dilute solution of a strong base is equal to the concentration of the base. For example, a 1.0 mol/L solution of sodium hydroxide (a strong base) contains 1.0 mol/L of hydroxide ions.

Table 10.5 lists some common strong bases. Barium hydroxide, Ba(OH)₂, and strontium hydroxide, Sr(OH)₂, are strong bases that are soluble in water. Magnesium oxide, MgO, and magnesium hydroxide, Mg(OH)2, are also strong bases, but they are considered to be insoluble. A small amount of these compounds does dissolve in water, however. Virtually all of this small amount dissociates completely.

Most bases are weak. A weak base dissociates very slightly in a water solution. The most common weak base is aqueous ammonia. In a 0.1 mol/L solution, only about 1% of the ammonia molecules react with water to form hydroxide ions. This reversible reaction is represented in Figure 10.9.

OH-

Figure 10.9 Ammonia does not contain hydroxide ions, so it is not an Arrhenius base. As you can see, however, an ammonia molecule can remove a proton from water, leaving a hydroxide ion behind. Thus, ammonia is a Brønsted-Lowry weak base.

Table 10.5 Common Strong Bases

| lanie 10.5 | Common Strong Dase |
|------------|--------------------------------|
| sodium h | ydroxide, NaOH |
| potassiur | n hydroxide, KOH |
| calcium l | nydroxide, Ca(OH) ₂ |
| strontiun | hydroxide, Sr(OH) ₂ |
| barium h | ydroxide, Ba(OH) ₂ |

CHECKPWINT

The terms "strong" and "concentrated" have very different meanings when describing solutions of acids, bases, or salts. Similarly, the terms "weak" and "dilute" have very different meanings. In your own words, summarize the difference between "strong" and "concentrated." Give examples that illustrate this difference. Then summarize the difference between "weak" and "dilute," again giving examples.



The conjugate base of a strong acid is always a weak base. Conversely, the conjugate base of a weak acid is always a strong base. Explain this inverse relationship.

Naming Acids and Their Anions

There are two main kinds of acids: binary acids and oxoacids. A binary acid is composed of two elements: hydrogen and a non-metal. Two examples of binary acids are hydrofluoric acid and hydrochloric acid. All binary acids have the general formula HX(aq). The H represents one or more hydrogen atoms. The X represents the non-metal. As you can see in Table 10.6, the names of binary acids are made up of the following parts:

- · the prefix hydro-
- · a root that is formed from the name of the non-metal
- · the suffix -ic
- · the word "acid" at the end

Table 10.6 Examples of Naming Binary Acids

| Binary acid | Prefix | Non-metal root | Suffix |
|--|--------|----------------|--------|
| hydrofluoric acid, HF(eq) | hydro- | -fluor- | -ic |
| hydrochloric acid, HCl _(aq) | hydro- | -chlor- | -ic |
| hydrosulfuric acid, H ₂ S | hydro- | -sulfur- | -ic |

As you know, anions are formed when binary acids dissociate. The names of these anions end in the suffix -ide. For example, hydroflouric acid forms the anion fluoride, F-. Hydrochloric acid forms the anion chloride, Cl.

An oxoacid is an acid formed from a polyatomic ion that contains oxygen, hydrogen, and another element. (Oxoacids are called oxyacids in some chemistry textbooks). In Chapter 3, you learned the names of common polyatomic ions and their valences (oxidation numbers). The names of oxoacids are similar to the names of their polyatomic oxoanions. Only the suffix is different. Study the three rules and examples for naming oxoacids below. Then try the Practice Problems that follow.

- 1. For anions that end in -ate, the suffix of the acid is -ic. For example. the acid of the chlorate anion ClO₃-, is chloric acid, HClO₃.
- 2. For anions that end in -ite, the suffix of the acid is -ous. For example, the acid of the chlorite anion, ClO_2^- , is chlorous acid, $HClO_2$.
- 3. The prefixes hypo- and per- remain as part of the acid name. For example, the acid of the perchlorate anion, ClO₄-, is perchloric acid, HClO₄. The acid of the hypochlorite anion, ClO, is hypochlorous acid, HClO.

Practice Problems

- 4. (a) Write the chemical formula for hydrobromic acid. Then write the name and formula for the anion that it forms.
 - (b) Hydrosulfuric acid, H2S, forms two anions. Name them and write their formulas.
- 5. Write the chemical formulas for the following acids. Then name and write the formulas for the oxoanions that form from each acid. Refer to Chapter 3, Table 3.5, Names and Valences of Some Common Polyatomic Ions, as necessary.
 - (a) nitric acid
- (d) phosphoric acid
- (b) nitrous acid
- (e) phosphorous acid
- (c) hyponitrous acid
- (f) periodic acid

Describing Acid and Base Strength Quantitatively: pH

You are probably familiar with the term "pH" from a variety of sources. Advertisers talk about the "pH balance" of products such as soaps, shampoos, and skin creams. People who own aquariums and swimming pools must monitor the pH of the water. (See Figure 10.10.) Gardeners and farmers use simple tests to determine the pH of the soil. They know that plants and food crops grow best within a narrow range of pH. Similarly, the pH of your blood must remain within narrow limits for you to stay healthy.



pH is clearly related to health, and to the proper functioning of products and systems. (Notice that the "p" is always lower case, even at the start of a sentence.) What exactly is pH? How is it measured? To answer these questions, consider a familiar substance: water.

Figure 10.10 Maintaining a safe environment for an aquarium or a swimming pool requires measuring the pH of the water and knowing how to adjust it.

The Power of Hydrogen in Water

As you know, all aqueous solutions contain ions. Even pure water contains a few ions that are produced by the dissociation of water molecules. **Remember:** The double arrow in the equation shows that the reaction is reversible. The ions recombine to form water molecules.

$$H_2O_{(\ell)} + H_2O_{(\ell)} \Rightarrow H_3O_{(aq)}^+ + OH_{(aq)}^-$$

On average, at 25°C, only about two water molecules in a billion are dissociated at any given moment. As you know, it is the ions in solution that conduct electricity. If there are virtually no ions, no electricity is conducted. This is why pure water is such a poor conductor. Chemists have determined that the concentration of hydronium ions in neutral water, at 25°C, is only 1.0×10^{-7} mol/L. The dissociation of water also produces the same, very small number of hydroxide ions. Therefore, the concentration of hydroxide ions is also 1.0×10^{-7} mol/L.

Chemists sometimes use square brackets around a chemical formula. This shorthand notation means "the concentration of" the chemical inside the brackets. For example, $[H_3O^+]$ is read as "the concentration of hydronium ions." Thus, the concentration of hydronium ions and hydroxide ions in neutral water can be written as

the concentration of hydronium ions
$$[H_3O^+]=[OH^-]=1.0\times 10^{-7}\,mol/L$$
 the concentration of hydroxide ions

Compared with neutral water, acidic solutions contain a higher concentration of hydronium ions. Basic solutions contain a lower concentration of hydronium ions. Therefore, the dissociation of water provides another way of thinking about acids and bases. An acid is any compound that increases [H₃O⁺] when it is dissalved in water. A base is any compound that increases [OH-] when it is dissolved in water. (See Figure 10.11.)



Figure 10.11 The relationship between the concentrations of hydronium ions and hydroxide ions in a solution determines whether the solution is acidic, basic, or neutral.

The pH Scale: Measuring by Powers of Ten

The concentration of hydronium ions ranges from about 10 mol/L for a concentrated strong acid to about 10-15 mol/L for a concentrated strong base. This wide range of concentrations, and the negative powers of 10. are not very convenient to work with. In 1909, a Danish biochemist, Søren Sørensen, suggested a method for converting concentrations to positive numbers. His method involved using the numerical system of logarithms.

The logarithm of a number is the power to which you must raise 10 to equal that number. For example, the logarithm of 10 is 1, because $10^1 = 10$. The logarithm of 100 is 2, because $10^2 = 100$. (See Appendix E for more information about exponents and logarithms.)

Sørensen defined pH as -log [H+]. Since Sørensen did not know ahout hydronium ions, his definition of pH is based on Arrhenius' hydrogen ion. Many chemistry references reinterpret the H so that it refers to the Brønsted-Lowry hydronium ion, H₃O⁺, instead. This textbook adopts the hydronium ion usage. Thus, the definition for pH becomes $pH = -log [H_3O^+]$. Recall, though, that chemists use $[H^+]$ as a shorthand notation for [H₃O⁺]. As a result, both equations give the same product.

As you can see in Figure 10.12, the "p" in pH stands for the word "power." The power referred to is exponential power: the power of 10. The "H" stands for the concentration of hydrogen ions (or H₃O⁺ ions), measured in mol/L.

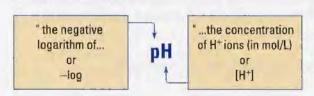


Figure 10.12 The concept of pH makes working with very small values, such as 0.000 000 000 000 01, much easier.

The concept of pH allows hydronium (or hydrogen) ion concentrations to be expressed as positive numbers, rather than negative exponents. For example, recall that $[H_3O^+]$ of neutral water at 25°C is 1.0×10^{-7} .

[H₃O⁺] in acidic solutions is greater than [H₃O⁺] in neutral water. For example, if $[H_3O^+]$ in an acid is 1.0×10^{-4} mol/L, this is 1000 times greater than [H₃O⁺] in neutral water. Use Table 10.7 to make sure that you understand why. The pH of the acid is 4.00. All acidic solutions have a pH that is less than 7.

Table 10.7 Understanding pH

| Range of acidity and basicity | [H ₃ 0 ⁺] (mol/L) | Exponential notation (mol/L) | log | pH (-log [H ₃ 0+]) |
|---|--|------------------------------|-----|----------------------------------|
| strong acid | 1 | 1×10^{0} | 0 | 0 |
| | 0.1 | 1×10^{-1} | -1 | 1 |
| | 0.01 | 1×10^{-2} | -2 | 2 |
| | 0.001 | 1×10^{-3} | -3 | 3 |
| | 0.000 1 | 1 × 10 ⁻⁴ | -4 | 4 |
| | 0.000 01 | 1×10^{-5} | -5 | 5 |
| | 0.000 001 | 1 × 10 ⁻⁶ | -6 | 6 |
| neutral $[H^+] = [OH^-]$ $= 1.0 \times 10^{-7}$ | 0.000 000 1 | 1 × 10 ⁻⁷ | -7 | 7 |
| | 0.000 000 01 | 1 × 10 ⁻⁸ | -8 | 8 |
| | 0.000 000 001 | 1×10^{-9} | -9 | 9 |
| | 0.000 000 000 1 | 1×10^{-10} | -10 | 10 |
| | 0.000 000 000 01 | 1 × 10 ⁻¹¹ | -11 | 11 |
| | 0.000 000 000 001 | 1×10^{-12} | -12 | 12 |
| | 0.000 000 000 000 1 | 1×10^{-13} | -13 | 13 |
| strong base | 0.000 000 000 000 01 | 1×10^{-14} | -14 | 14 |

[H₃O⁺] in basic solutions is less than [H₃O⁺] in pure water. For example, if $[H_3O^+]$ in a base is 1.0×10^{-11} mol/L, this is 10 000 times less than [H₃O⁺] in neutral water. The pH of the base is 11.00. All basic solutions have a pH that is greater than 7.

The relationship among pH, [H₃O⁺], and the strength of acids and bases is summarized in the Concept Connection on the next page. Use the following Sample Problem and Practice Problems to assess your understanding of this relationship. Then, in Investigation 10-A, you will look for a pattern involving the pH of a strong acid, a weak acid, and dilutions of both.

Science

Using logarithms is a convenient way to count a wide range of values by powers of 10. Chemists are not the only scientists who use such logarithms, however. Audiologists (scientists who study human hearing) use logarithms, too. Research the decibel scale to find out how it works. Present your findings in the medium of your choice.

Math LINK

How do you determine the number of significant digits in a pH? You count only the digits to the right of the decimal point. For example, suppose that the concentration of hydronium ions in a sample of orange juice is 2.5×10^{-4} mol/L. This number has two significant digits: the 2 and the 5. The power of 10 only tells us where to place the decimal: 0.000 25. The pH of the sample is $-\log (2.5 \times 10^{-4}) = 3.602 059.$ The digit to the left of the decimal (the 3) is derived from the power of 10. Therefore, it is not considered to be a significant digit. Only the two digits to the right of the decimal are significant. Thus, the pH value is rounded off to 3.60.

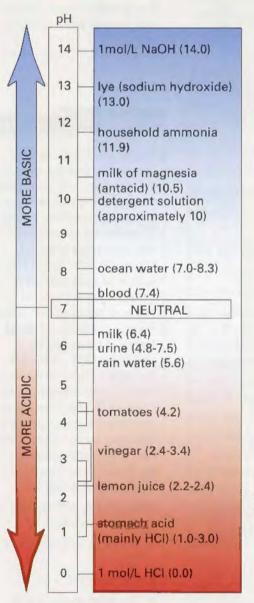
Identify the significant digits in each pH value below.

- 1. The pH of drain cleaner is 13.1.
- 2. The pH of milk is 6.4.
- 3. The pH of vinegar is 2.85.
- 4. The pH of lemon juice is 2.310.

Concept Organizer

pH, [H₃O⁺], and the Strength of Acids and Bases

| Type of solution | [H ₃ 0+] (mol/L) | Concentration of hydronium and hydroxide ions | pH at 25°C |
|------------------|---------------------------------|---|------------|
| acidic solution | greater than 1×10^{-7} | $[H_3O^+] > [OH^-]$ | < 7.00 |
| neutral solution | 1×10^{-7} | $[H_3O^+] = [OH^-]$ | 7.00 |
| basic solution | less than 1×10^{-7} | [H ₃ O ⁺] < [OH ⁻] | > 7.00 |





The pH values of many common solutions fall within a range from 0 to 14, as shown on this pH scale. The table above the pH scale relates the positive pH values to their hydronium ion concentrations and their logarithms.

Sample Problem

Calculating the pH of a Solution

Problem

Calculate the pH of a solution with $[H_3O^+] = 3.8 \times 10^{-3}$ mol/L.

What Is Required?

You need to calculate the pH, given [H₃O⁺].

What Is Given?

You know that $[H_3O^+]$ is 3.8×10^{-3} mol/L.

Plan Your Strategy

Use the equation $pH = -log [H_3O^+]$ to solve for the unknown.

Act on Your Strategy

$$pH = -log (3.8 \times 10^{-3})$$

= 2.42

Check Your Solution

 $[H_3O^+]$ is greater than 1.0×10^{-7} mol/L. Therefore, the pH should be less than 7.00. The solution is acidic, as you would expect.

Practice Problems

- 6. Calculate the pH of each solution, given the hydronium ion concentration.
 - (a) $[H_3O^+] = 0.0027 \text{ mol/L}$
 - **(b)** $[H_3O^+] = 7.28 \times 10^{-8} \text{ mol/L}$
 - (c) $[H_3O^+] = 9.7 \times 10^{-5} \text{ mol/L}$
 - (d) $[H_3O^+] = 8.27 \times 10^{-12}$
- 7. $[H_3O^+]$ in a cola drink is about 5.0×10^{-3} mol/L. Calculate the pH of the drink. State whether the drink is acidic or basic.
- 8. A glass of orange juice has $[H_3O^+]$ of 2.9×10^{-4} mol/L. Calculate the pH of the juice. State whether the result is acidic or basic.
- 9. (a) [H₃O⁺] in a dilute solution of nitric acid, HNO₃, is 6.3×10^{-3} mol/L. Calculate the pH of the solution.
 - (b) $[H_3O^+]$ of a solution of sodium hydroxide is 6.59×10^{10} mol/L. Calculate the pH of the solution.

Appendix E, "Math and Chemistry", explains how you can do these calculations with a calculator.

Investigation 10-A

SKILL FOCUS

Predicting

Performing and recording

Analyzing and interpreting

The Effect of Dilution on the pH of an Acid

In this investigation, you will compare the effects of diluting a strong acid and a weak acid.

In Part 1, you will measure the pH of a strong acid. Then you will perform a series of ten-fold dilutions. That is, each solution will be one-tenth as dilute as the previous solution. You will measure and compare the pH after each dilution.

In Part 2, you will measure the pH of a weak acid with the same initial concentration as the strong acid. Then you will perform a series of ten-fold dilutions with the weak acid. Again, you will measure and compare the pH after each dilution.

Problem

How does the pH of dilutions of a strong acid compare with the pH of dilutions of a weak acid?

Prediction

Predict each pH, and explain your reasoning. (a) the pH of 0.10 mol/L hydrochloric acid

- (b) the pH of the hydrochloric acid after one ten-fold dilution
- (c) the pH of the hydrochloric acid after each of six more ten-fold dilutions
- (d) the pH of 0.10 mol/L acetic acid, compared with the pH of 0.10 mol/L hydrochloric acid
- (e) the pH of the acetic acid after one ten-fold dilution

Safety Precautions



Hydrochloric acid is corrosive. Wash any spills on skin or clothing with plenty of cool water. Inform your teacher immediately.

Materials

100 mL graduated cylinder 100 mL beaker 2 beakers (250 mL) universal indicator paper and glass rod pH meter 0.10 mol/L hydrochloric acid (for Part 1) 0.10 mol/L acetic acid (for Part 2) distilled water

Procedure

Part 1 The pH of Solutions of a Strong Acid

- 1. Copy the table below into your notebook. Record the pH you predicted for each dilution.
- 2. Pour about 40 mL of 0.10 mol/L hydrochloric acid into a clean, dry 100 mL beaker. Use the end of a glass rod to transfer a drop of solution to a piece of universal pH paper into the acid. Compare the colour against the colour chart to determine the pH. Record the pH. Then measure and record the pH of the acid using a pH meter. Rinse the electrode with distilled water afterward.

Data Table for Part 1

| [HCl _(aq)] mol/L | Predicted pH | pH measured with universal indicator | pH measured with pH meter |
|------------------------------|--------------|--------------------------------------|---------------------------|
| 1×10^{-1} | | | |
| 1×10^{-2} | | | |
| 1×10^{-3} | | | |
| 1×10^{-4} | | | |
| 1×10^{-5} | | | |
| 1×10^{-6} | | | |
| 1×10^{-7} | | | |
| 1×10^{-8} | | | |



- 3. Measure 90 mL of distilled water in a 100 mL graduated cylinder. Add 10 mL of the acid from step 2. The resulting 100 mL of solution is one-tenth as concentrated as the acid from step 2. Pour the dilute solution into a clean, dry 250 mL beaker. Use universal pH paper and a pH meter to measure the pH. Record your results.
- 4. Repeat step 3. Pour the new dilute solution into a second clean, dry beaker. Dispose of the more concentrated acid solution as directed by your teacher. Rinse and dry the beaker so you can use it for the next dilution.
- 5. Make further dilutions and pH measurements until the hydrochloric acid solution is $1.0 \times 10^{-8} \text{ mol/L}$

Part 2 The pH of Solutions of a Weak Acid

- 1. Design a table to record your predictions and measurements for 0.10 mol/L and 0.010 mol/L concentrations of acetic acid.
- 2. Use the same procedure that you used in Part 1 to measure and record the pH of a 0.10 mol/L sample of acetic acid. Then dilute the solution to 0.010 mol/L. Measure the pH again.

Analysis

- 1. Which do you think gave the more accurate pH: the universal indicator paper or the pH meter? Explain.
- 2. For the strong acid, compare the pH values you predicted with the measurements you made. How can you explain any differences for the first few dilutions?

- 3. What was the pH of the solution that had a concentration of 1.0×10^{-8} mol/L? Explain the pH you obtained.
- 4. Compare the pH of 0.10 mol/L acetic acid with the pH of 0.10 mol/L hydrochloric acid. Why do you think the pH values are different, even though the concentrations of the acids were the same?
- 5. What effect does a ten-fold dilution of a strong acid (hydrochloric acid) have on the pH of the acid? What effect does the same dilution of a weak acid (acetic acid) have on its pH? Compare the effects for a strong acid and a weak acid. Account for any differences.

Conclusion

- 6. Use evidence from your investigation to support the conclusion that a weak acid dissociates less than a strong acid of identical concentration.
- 7. Why is the method for calculating the pH of a strong acid (if it is not too dilute) not appropriate for a weak acid?

Applications

- 8. Nicotinic acid is a B vitamin. The pH of a 0.050 mol/L solution of this acid is measured to be 3.08. Is it a strong acid or a weak acid? Explain. What would be the pH of a solution of nitric acid having the same concentration?
- 9. Would you expect to be able to predict the pH of a weak base, given its concentration? Design an experiment you could perform to check your answer.

Chemistry Bulletin

Science

Technology

Society

Environment

The Chemistry of Oven Cleaning



Oven cleaning is not a job that most people enjoy. Removing baked-on grease from inside an oven requires serious scrubbing. Any chemical oven cleaners that help to make the job easier are usually welcome. Like all chemicals, however, the most effective oven cleaners require attention to safety.

Cleaners that contain strong bases are the most effective for dissolving grease and grime. Bases are effective because they produce soaps when they react with the fatty acids in grease. When a strong base (such as sodium hydroxide, NaOH, or potassium hydroxide, KOH) is used on a dirty oven, the fat molecules that make up the grease are split into smaller molecules. Anions from the base then bond with some of these molecules to form soap.

One end of a soap molecule is non-polar (uncharged), so it is soluble in dirt and grease, which are also non-polar. The other end of a soap molecule is polar (charged), so it is soluble in water. Because of its two different properties, soap acts like a "bridge" between the grease and the water. Soap enables grease to dissolve in water and be washed away, thus allowing the cleaner to remove the grease from the oven surface.

Cleaners that contain sodium hydroxide and potassium hydroxide are very effective. They are also caustic and potentially very dangerous. For example, sodium hydroxide, in the concentrations that are used in oven cleaners, can irritate the skin and cause blindness if it gets in the eyes. As well, it is damaging to paints and fabrics.

There are alternatives to sodium hydroxide and other strong base cleaners. One alternative involves using ammonia, NH₃, which is a weak base. If a bowl of dilute ammonia solution is placed in an oven and left for several hours, most of the grease and grime can be wiped off.

Ammonia does not completely ionize in water. Only a small portion dissociates.

Although an ammonia solution is less caustic than sodium hydroxide, it can be toxic if inhaled directly. As well, ammonia vapours can cause eye, lung, and skin irritations. At higher concentrations, ammonia can be extremely toxic.

Baking soda is a non-toxic alternative, but it is much less effective. Therefore, it requires even more scrubbing. An abrasive paste can be made by mixing baking soda and water. The basic properties of baking soda also have a small effect on grease and grime if it is applied to the oven and left for several hours.

Making Connections

- 1. Survey the cleaners in your home or school. Which cleaners contain bases and which contain acids? What cleaning jobs can an acid cleaner perform well? How do most acid cleaners work?
- 2. Some companies claim to make environmentally sensitive cleaners. Investigate these cleaners. What chemicals do they contain? See if you can infer how they work. You might like to design a controlled experiment to test the effectiveness of several oven cleaners. CAUTION Obtain permission from your teacher before performing such an experiment.

Section Wrap-up

In this section, you considered the relationship among the strength of acids and bases, the concentration of hydronium and hydroxide ions, and pH. Much of the time, you examined acids and bases acting independently of each other. However, acids and bases often interact. In fact, acid-base reactions have many important applications in the home, as well as in the laboratory. In section 10.3, you will investigate acid-base reactions.

Section Review

- ① KTD Distinguish, in terms of degree of dissociation, between a strong acid and a weak acid, and a strong base and a weak base.
- 2 Give one example of the following:
 - (a) a weak acid
 - (b) a strong acid
 - (c) a strong base
 - (d) a weak base
- 3 K/D Formic acid, HCOOH, is responsible for the painful bites of fire ants. Is formic acid strong or weak? Explain.
- 4 KMnO₄ is an intense purple-coloured solid that can be made into a solution to kill bacteria. What is the name of this compound?

 Give the name and the formula of the acid that forms when KMnO₄ combines with water.
- 5 State the name or the formula for the acid that forms from each of the following anions:
 - (a) hydrogen sulfate
 - (b) F
 - (c) HS-
 - (d) bromite
- 6 Explain the meaning of pH, both in terms of hydrogen ions and hydronium ions.
- Arrange the following foods in order of increasing acidity: beets, pH = 5.0; camembert cheese, pH = 7.4; egg white, pH = 8.0; sauerkraut, pH = 3.5; yogurt, pH = 4.5.
- - (a) tears, $[H_3O^+] = 4.0 \times 10^{-8} \text{ mol/L}$
 - (b) stomach acid, $[H_3O^+] = 4.0 \times 10^{-2} \text{ mol/L}$
- ① Calculate the pH of the solution that is formed by diluting 50 mL of 0.025 mol/L hydrochloric acid to a final volume of 1.0 L
- What is $[H_3O^+]$ in a solution with pH = 0? Why do chemists not usually use pH to describe $[H_3O^+]$ when the pH value would be a negative number?

Unit Issue Prep

As you investigate the contamination of Prince Edward Island's soils with sodium arsenite from pesticides, investigate the link between the pH and solubility. For example, water polluted with sodium arsenite may be treated with lime (calcium oxide), CaO. What is the purpose of this treatment?

10.3

Acid-Base Reactions

Section Preview/ Specific Expectations

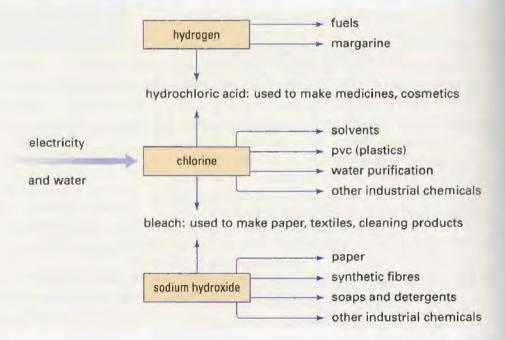
In this section, you will

- perform calculations involving neutralization reactions
- determine the concentration of an acid in solution by conducting a titration
- communicate your understanding of the following terms: neutralization reaction, salt, acid-base indicator, titration, equivalence point, end-point

Is there a box of baking soda in your refrigerator at home? Baking soda is sodium hydrogen carbonate. (It is also commonly called sodium bicarbonate.) Baking soda removes the odours caused by spoiling foods. The smelly breakdown products of many foods are acids. Baking soda, a base, eliminates the odours by neutralizing the characteristic properties of the acids.

Adding a base to an acid neutralizes the acid's acidic properties. This type of reaction is called a neutralization reaction.

There are many different acids and bases. Being able to predict the results of reactions between them is important. Bakers, for example, depend on neutralization reactions to create light, fluffy baked goods. Gardeners and farmers depend on these reactions to modify the characteristics of the soil. Industrial chemists rely on these reactions to produce the raw materials that are used to make a wide variety of chemicals and chemical products. (See Figure 10.13.)



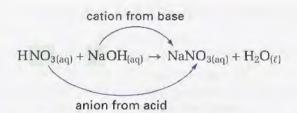
salt (sodium chloride)

Figure 10.13 You know sodium chloride as common table salt. As you can see here, however, sodium chloride is anything but common. Sodium chloride is a product of an acid-base reaction between hydrochloric acid and sodium hydroxide.

Neutralization Reactions

The reaction between an acid and a base produces an ionic compound (a salt) and water.

A salt is an ionic compound that is composed of the anion from an acid and a cation from a base. For example, sodium nitrate is a salt that is found in many kitchens. It is often added to processed meat to preserve the colour and to slow the rate of spoiling by inhibiting bacterial growth. Sodium nitrate can be prepared in a laboratory by reacting nitric acid with sodium hydroxide, as shown on the next page.



The balanced chemical equation for this reaction shows that 1 mol of nitric acid reacts with 1 mol of sodium hydroxide. If equal molar quantities of nitric acid and sodium hydroxide are used, the result is a neutral (pH 7) aqueous solution of sodium nitrate. In fact, when any strong acid reacts with any strong base in the mole ratio from the balanced chemical equation, a neutral aqueous solution of a salt is formed. Reactions between acids and bases of different strengths usually do not result in neutral solutions.

For most neutralization reactions, there are no visible signs that a reaction is occurring. How can you determine that a neutralization reaction is taking place? One way is to use an acid-base indicator. This is a substance that changes colour in acidic and basic solutions. Most acid-base indicators are weak, monoprotic acids. The undissociated weak acid is one colour. Its conjugate base is a different colour.

$$\begin{array}{c} & \text{colour 1} \\ \text{H (indicator)}_{(aq)} & \rightleftharpoons & \text{H}^+ + \text{ (indicator)}_{(aq)} \\ & \text{colour 2} & & \\ \end{array}$$

In an acidic solution, the indicator does not dissociate very much. It appears as colour 1. In a basic solution, the indicator dissociates much more. It appears as colour 2. Often a single drop of indicator causes a dramatic change in colour. For example, phenolphthalein is an indicator that chemists often use for reactions between a strong acid and a strong base. It is colourless between pH 0 and pH 8. It turns pink between pH 8 and pH 10. (See Figure 10.14.)



Figure 10.14 A good indicator, such as the phenolphthalein shown here, must give a vivid colour change.



If a small quantity of an acid or a base is spilled in a laboratory, you can use a neutralization reaction to minimize the hazard. To neutralize a basic solution spill, you can add solid sodium hydrogen sulfate or citric acid. For an acidic solution spill, you can use sodium hydrogen carbonate (baking soda). Note that you cannot use a strong acid or base to clean up a spill. This would result in another hazardous spill. As well, the neutralization reaction would generate a lot of heat, and thus produce a very hot solution.

CHECKPOINT

Show that the net ionic equation for the reaction between HNO3 (a strong acid) and NaOH (a strong base) results in the formation of water.



An old remedy to relieve the prickly sting of a nettle plant is to rub the area with the leaf of a dock plant. The sting contains an acid. This acid is neutralized by a base that is present in the dock leaf. Bees and ants also have an acidic sting. You can wash the sting with soap, because soap is basic. You can also apply baking soda (a base) to the skin for more effective relief. If you are stung by a wasp, however, you should apply vinegar. The sting of a wasp contains a base.

PROBLEM TIPS

- 1. Make sure that the values you use in your calculations refer to the same reactant. For example, you can use the concentration and volume of sodium hydroxide to find the amount of sodium hydroxide in this problem. You cannot use the concentration of sodium hydroxide and the volume of hydrochloric acid.
- In the solution, the volumes are converted to litres. If all the volumes are expressed in the same unit, the conversion step is not necessary.
- Do not drop significant digits, even zeros, during your calculations.

Calculations Involving Neutralization Reactions

Suppose that a solution of an acid reacts with a solution of a base. You can determine the concentration of one solution if you know the concentration of the other. (This assumes that the volumes of both are accurately measured.) Use the concentration and volume of one solution to determine the amount (in moles) of reactant that it contains. The balanced chemical equation for the reaction describes the mole ratio in which the compounds combine. In the following Sample Problems and Practice Problems, you will see how to do these calculations.

Sample Problem

Finding Concentration

Problem

13.84 mL of hydrochloric acid, $HCl_{(aq)}$, just neutralizes 25.00 mL of a 0.1000 mol/L solution of sodium hydroxide, $NaOH_{(aq)}$. What is the concentration of the hydrochloric acid?

What Is Required?

You need to find the concentration of the hydrochloric acid.

What Is Given?

Volume of hydrochloric acid, HCl = 13.84 mLVolume of sodium hydroxide, NaOH = 25.00 mLConcentration of sodium hydroxide, NaOH = 0.1000 mol/L

Plan Your Strategy

- Step 1 Write the balanced chemical equation for the reaction.
- Step 2 Calculate the amount (in mol) of sodium hydroxide added, based on the volume and concentration of the sodium hydroxide solution.
- Step 3 Determine the amount (in mol) of hydrochloric acid needed to neutralize the sodium hydroxide.
- Step 4 Find $[HCl_{(aq)}]$, based on the amount and volume of hydrochloric acid solution needed.

Act on Your Strategy

Step 1 The balanced chemical equation is

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(\ell)}$$

Step 2 Amount (in mol) = Concentration (in mol/L)

× Volume (in L)

Amount NaOH (in mol) added = $0.1000 \text{ mol/L} \times 0.02500 \text{ L}$

 $= 2.500 \times 10^{-3} \text{ mol}$

Continued ..

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Continued ...
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Step 3 HCl reacts with NaOH in a 1:1 ratio, so there must be 2.500×10^{-3} mol HCl.

Step 4 Concentration (in mol/L) = $\frac{\text{Amount (in mol)}}{\text{Volume (in L)}}$ $[HCl_{(aq)}] = \frac{2.500 \times 10^3 \text{ mol}}{0.01384 \text{ L}}$ = 0.1806 mol/L

Therefore, the concentration of hydrochloric acid is 0.1806 mol/L.

Check Your Solution

 $[HCl_{(aq)}]$ is greater than $[NaOH_{(aq)}]$. This is reasonable because a smaller volume of hydrochloric acid was required. As well, the balanced equation shows a 1:1 mole ratio between these reactants.

Sample Problem

Finding Volume

Problem

What volume of 0.250 mol/L sulfuric acid, $H_2SO_{4(aq)}$, is needed to react completely with 37.2 mL of 0.650 mol/L potassium hydroxide, $KOH_{(aq)}$?

What Is Required?

You need to find the volume of sulfuric acid.

What Is Given?

Concentration of sulfuric acid, $H_2SO_4 = 0.250 \text{ mol/L}$ Concentration of potassium hydroxide, KOH = 0.650 mol/L Volume of potassium hydroxide, KOH = 37.2 mL.

Plan Your Strategy

- Step 1 Write the balanced chemical equation for the reaction.
- Step 2 Calculate the amount (in mol) of potassium hydroxide, based on the volume and concentration of the potassium hydroxide solution.
- Step 3 Determine the amount (in mol) of sulfuric acid that is needed to neutralize the potassium hydroxide.
- Step 4 Find the volume of the sulfuric acid, based on the amount and concentration of sulfuric acid needed.

Act on Your Strategy

Step 1 The balanced chemical equation is

$$H_2SO_{4(aq)} + 2KOH \rightarrow K_2SO_{4(aq)} + 2H_2O_{(\ell)}$$

Step 2 Amount (in mol) of KOH = $0.650 \text{ mol/L} \times 0.0372 \text{ L}$ = 0.02418 mol

Continued .



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Step 3 H₂SO₄ reacts with KOH in a 1:2 mole ratio. The amount of H₂SO₄ needed is

 $\frac{1 \text{ mol H}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4} = \frac{0.01209 \text{ mol H}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4}$ 2 mol KOH 0.2418 mol KOH

 $0.024\ 18\ mol\ KOH \times 1\ mol\ H_2SO_4 = 0.01209\ mol\ H_2SO_4$ 2 mol KOH

Step 4 Amount (in mol) H2SO4

= 0.01209 mol

= $0.250 \text{ mol/L} \times \text{Volume H}_2\text{SO}_{4(ag)}$ (in L)

Volume $H_2SO_{4(aq)} = \frac{0.01209 \text{ mol}}{0.01209 \text{ mol}}$ = 0.04836 L

Therefore, the volume of sulfuric acid that is needed is 48.4 mL.

Check Your Solution

The balanced chemical equation shows that half the amount of sulfuric acid will neutralize a given amount of potassium hydroxide. The concentration of sulfuric acid, however, is less than half the concentration of potassium hydroxide. Therefore, the volume of sulfuric acid should be greater than the volume of potassium hydroxide.

Practice Problems

- 10. 17.85 mL of nitric acid neutralizes 25.00 mL of 0.150 mol/L NaOH_(an). What is the concentration of the nitric acid?
- 11. What volume of 1.015 mol/L magnesium hydroxide is needed to neutralize 40.0 mL of 1.60 mol/L hydrochloric acid?
- 12. What volume of 0.150 mol/L hydrochloric acid is needed to neutralize each solution below?
 - (a) 25.0 mL of 0.135 mol/L sodium hydroxide
 - (b) 20.0 mL of 0.185 mol/L ammonia solution
 - (c) 80 mL of 0.0045 mol/L calcium hydroxide
- 13. What concentration of sodium hydroxide solution is needed for each neutralization reaction?
 - (a) 37.82 mL of sodium hydroxide neutralizes 15.00 mL of 0.250 mol/L hydrofluoric acid.
 - (b) 21.56 mL of sodium hydroxide neutralizes 20.00 mL of 0.145 mol/L sulfuric acid.
 - (c) 14.27 mL of sodium hydroxide neutralizes 25.00 mL of 0.105 mol/L phosphoric acid.

Acid-Base Titration

In the previous Sample Problems and Practice Problems, you were given the concentrations and volumes you needed to solve the problems. What if you did not have some of this information? Chemists often need to know the concentration of an acidic or basic solution. To acquire this information, they use an experimental procedure called a titration. In a titration, the concentration of one solution is determined by quantitatively observing its reaction with a solution of known concentration. The solution of known concentration is called a standard solution. The aim of a titration is to find the point at which the number of moles of the standard solution is stoichiometrically equal to the original number of moles of the unknown solution. This point is referred to as the equivalence point. At the equivalence point, all the moles of hydrogen ions that were present in the original volume of one solution have reacted with an equal number of moles of hydroxide ions from the other solution.

Precise volume measurements are needed when you perform a titration. Chemists use special glass apparatus to collect these measurements. (See Figure 10.15.) As well, an acid-base indicator is needed to monitor changes in pH during the titration.



Figure 10.15 A transfer pipette (bottom) measures a fixed volume of liquid, such as 10.00 mL, 25.00 mL, or 50.0 mL. A burette (top) measures a variable volume of liquid.

In a titration, a pipette is used to measure a precise volume of standard solution into a flask. The flask sits under a burette that contains the solution of unknown concentration. After adding a few drops of indicator, you take an initial burette reading. Then you start adding the known solution, slowly, to the flask. The end-point of the titration occurs when the indicator changes colour. The indicator is chosen so that it matches its equivalance point.

Titration Step by Step

The following pages outline the steps that you need to follow to prepare for a titration. Review these steps carefully. Then observe as your teacher demonstrates them for you. At the end of this section, in Investigation 10-B, you will perform your own titration of a common substance: vinegar.

Web LINK

www.school.mcgrawhill.ca/ resources

Sometimes a moving picture is worth a thousand words. To enhance your understanding, your teacher will demonstrate the titration procedure described in this textbook. In addition, some web sites provide downloadable or real-time titration movies to help students visualize the procedure and its techniques. Go to the web site above, then to Science Resources and to Chemistry 11 to see where to go next. Compare the different demonstrations you can find and observe, including your teacher's. Prepare your own set of "Titration Tips" to help you recall important details.

PROBEWARE

If you have access to probeware, try the Chemistry 11 lab, Titrating an Unknown, or a similar lab from a probeware company

TITRATION TIP

Never use your mouth in place of a suction bulb to draw a liquid into a pipette. The liquid could be corrosive or poisonous. As well, you will contaminate the glass stem.

TITRATION TIP

Practice removing the bulb and replacing it with your index finger (or thumb). You need to be able to perform this action quickly and smoothly.



Figure 10.18 You can prevent a "stubborn" drop from clinging to the pipette tip by touching the tip to the inside of the glass surface.

Rinsing the Pipette

A pipette is used to measure and transfer a precise volume of liquid. You rinse a pipette with the solution whose volume you are measuring. This ensures that any drops that remain inside the pipette will form part of the measured volume.

- 1. Pour a sample of standard solution into a clean, dry beaker.
- 2. Place the pipette tip in a beaker of distilled water. Squeeze the suction bulb. Maintain your grip while placing it over the stem of the pipette. Do not insert the stem into the bulb. (If your suction bulbs have valves, your teacher will show you how to use them.)
- 3. Relax your grip on the bulb to draw up a small volume of distilled water.
- 4. Remove the bulb and discard the water by letting it drain out.
- 5. Rinse the pipette by drawing several millilitres of solution from the beaker into it. Rotate and rock the pipette to coat the inner surface with solution. Discard the rinse. Rinse the pipette twice in this way. It is now ready to fill with standard solution.

Filling the Pipette

- 6. Place the tip of the pipette below the surface of the solution.
- 7. Hold the suction bulb loosely on the end of the glass stem. Use the suction bulb to draw liquid up just past the etched volume mark. (See Figure 10.16.)
- 8. As quickly and smoothly as you can, slide the bulb off and place your index finger over the end of the glass stem.
- 9. Gently roll your finger slightly away from end of the stem to let solution drain slowly out.
- 10. When the bottom of the meniscus aligns with the etched mark, as in Figure 10.17, press your finger back over the end of the stem. This will prevent more solution from draining out.
- 11. Touch the tip of the pipette to the side of the beaker to remove any clinging drop. See Figure 10.18. The measured volume inside the pipette is now ready to transfer to an Erlenmeyer flask or a volumetric flask.

Transferring the Solution

- 12. Place the tip of the pipette against the inside glass wall of the flask. Let the solution drain slowly, by removing your finger from the stem.
- 13. After the solution drains, wait several seconds, then touch the tip to the inside wall of the flask to remove any drop on the end. Note: You may notice a small amount of liquid remaining in the tip. The pipette was calibrated to retain this amount. Do not try to remove it.



Figure 10.16 Draw a bit more liquid than you need into the pipette. It is easier to reduce this volume than it is to add more solution to the pipettes.



Figure 10.17 The bottom of the meniscus must align exactly with the etched mark.

Adding the Indicator

14. Add two or three drops of indicator to the flask and its contents. Do not add too much indicator. Using more does not make the colour change easier to see. Also, indicators are usually weak acids. Too much can change the amount of base needed for neutralization. You are now ready to prepare the apparatus for the titration.

Rinsing the Burette

A burette is used to accurately measure the volume of liquid added during a titration experiment. It is a graduated glass tube with a tap at one end.

- 15. To rinse the burette, close the tap and add about 10 mL of distilled water from a wash bottle.
- 16. Tip the burette to one side and roll it gently back and forth so that the water comes in contact with all inner surfaces.
- 17. Hold the burette over a sink. Open the tap, and let the water drain out. While you do this, check that the tap does not leak. Make sure that it turns smoothly and easily.
- 18. Rinse the burette with 5 ml to 10 ml of the solution that will be measured. Remember to open the tap to rinse the lower portion of the burette. Rinse the burette twice, discarding the liquid each time.

Filling the Burette

- 19. Assemble a retort stand and burette clamp to hold the burette. Place a funnel in the top of the burette
- 20. With the tap closed, add solution until the liquid is above the zero mark. Remove the funnel. Carefully open the tap. Drain the liquid into a beaker until the bottom of the meniscus is at or below the zero mark.
- 21. Touch the tip of the burette against the beaker to remove any clinging drop. Check that the portion of the burette that is below the tap is filled with liquid and contains no air bubbles.
- 22. Record the initial burette reading in your
- 23. Replace the beaker with the Erlenmeyer flask that you prepared earlier. Place a sheet of white paper under the Erlenmeyer to help you see the indicator colour change that will occur near the end-point.

Reading the Burette

24. A meniscus reader is a small white card with a thick black line on it. Hold the card behind the burette, with the black line just under the meniscus, as in Figure 10.20. Record the volume added from the burette to the nearest 0.05 mL.

TITRATION TIP

If you are right-handed, the tap should be on your right as you face the burette. Use your left hand to operate the tap. Use your right hand to swirl the liquid in the Erlenmeyer flask. If you are left-handed, reverse this arrangement.



TITRATION TIP

Near the end-point, when you see the indicator change colour as liquid enters the flask from the burette, slow the addition of liquid. The endpoint can occur very quickly.



Figure 10.20 A meniscus reader helps you read the volume of liquid in the burette more easily

TITRATION TIP

Observe the level of solution in the burette so that your eye is level with the bottom of the meniscus

Investigation 10-B

SKILL FOCUS

Predicting

Performing and recording

Analyzing and interpreting

The Concentration of Acetic Acid in Vinegar

Vinegar is a dilute solution of acetic acid, CH3COOH. Only the hydrogen atom that is attached to an oxygen atom is acidic. Thus, acetic acid is monoprotic. As a consumer, you can buy vinegar with different concentrations. For example, the concentration of table vinegar is different from the concentration of the vinegar that is used for pickling foods. To maintain consistency and quality, manufacturers of vinegar need to determine the percent concentration of acetic acid in the vinegar. In this investigation, you will determine the concentration of acetic acid in a sample of vinegar.

Prediction

Which do you predict has the greater concentration of acetic acid: table vinegar or pickling vinegar? Give reasons for your prediction.

Materials

pipette suction bulb retort stand burette burette clamp 3 beakers (250 mL) 3 Erlenmeyer flasks (250 mL) labels meniscus reader sheet of white paper funnel table vinegar pickling vinegar sodium hydroxide solution distilled water dropper bottle containing phenolphthalein

Safety Precautions







Both vinegar and sodium hydroxide solutions are corrosive. Wash any spills on skin or clothing with plenty of water. Inform your teacher immediately.

Procedure

- 1. Record the following information in your notebook. Your teacher will tell you the concentration of the sodium hydroxide solution.
 - concentration of NaOH_(aq) (in mol/L)
 - · type of vinegar solution
 - volume of pipette (in mL)
- 2. Copy the table below into your notebook, to record your observations.

Burette Readings for the Titration of Acetic Acid

| Reading (mL) | Trial 1 | Trial 2 | Trial 3 |
|-----------------|---------|---------|---------|
| final reading | | | |
| initial reading | | | |
| volume added | | | |

- 3. Label a clean, dry beaker for each liquid: NaOH(aq), vinegar, and distilled water. Obtain each liquid. Record the type of vinegar you will be testing.
- 4. Obtain a pipette and a suction bulb. Record the volume of the pipette for trial 1. Rinse it with distilled water, and then with vinegar.
- 5. Pipette some vinegar into the first Erlenmeyer flask. Record this amount. Add approximately 50 mL of water. Also add two or three drops of phenolphthalein indicator.
- 6. Set up a retort stand, burette clamp, burette, and funnel. Rinse the burette first with distilled water. Then rinse it with sodium hydroxide solution. Make sure that there are no air bubbles in the burette. Also make sure

- that the liquid fills the tube below the glass tap. Remove the funnel before beginning the titration.
- 7. Place a sheet of white paper under the Erlenmeyer flask. Titrate sodium hydroxide into the Erlenmeyer flask while swirling the contents. The end-point of the titration is reached when a permanent pale pink colour appears. If you are not sure whether you have reached the end-point, take the burette reading. Add one drop of sodium hydroxide, or part of a drop. Observe the colour of the solution. If you go past the end-point, the solution will become quite pink.
- 8. Repeat the titration twice more. Record your results for each of these trials.
- 9. When you have finished all three trials, dispose of the chemicals as directed by your teacher. Rinse the pipette and burette with distilled water. Leave the burette tap open.

Analysis

- Average the two closest burette readings.
 Average all three readings if they agree within about ±0.2 mL.
- 2. Write the chemical equation for the reaction of acetic acid with sodium hydroxide.
- Calculate the concentration of acetic acid in your vinegar sample. Use the average volume and concentration of sodium hydroxide, and the volume of vinegar.
- Find the molar mass of acetic acid. Then calculate the mass of acid in the volume of vinegar you used.
- 5. The density of vinegar is 1.01 g/mL. (The density of the more concentrated vinegar solution is greater than the density of the less concentrated solution. You can ignore the difference, however.) Calculate the mass of the vinegar sample. Find the percent hy mass of acetic acid in the sample.

Conclusions

- 6. Compare your results with the results of other students who used the same type of vinegar. Then compare the concentration of acetic acid in table vinegar with the concentration in pickling vinegar. How did your results compare with your prediction?
- 7. List several possible sources of error in this investigation.

Application

9. Most shampoos are basic. Why do some people rinse their hair with vinegar after washing it?

Section Wrap-up

In this section, as in much of Unit 3, you combined liquid solutes and liquid solvents. You have learned how to describe the concentration of ions that determine the acidic or basic nature of a solution. As well, you performed calculations to determine the concentration of acids and many other substances in solution. In the upcoming unit, you will apply your understanding of stoichiometry and solutions by examining the nature and interactions of substances in the gaseous state.

Section Review

- 1 WD Write a generalized word equation to describe what happens during a neutralization reaction.
- 2 KD Write a chemical equation for each neutralization reaction.
 - (a) KOH with HNO3
 - (b) HBr with Ca(OH)2
 - (c) H₃PO₄ with NaOH
 - (d) Mg(OH)₂ (the active ingredient in milk of magnesia, an antacid) with HCl (the acid in your stomach)
- 3 KD Distinguish between the equivalence point and the end-point in a titration. Why might they be different? How would this affect the result of a titration?
- 🗿 💶 A 25.0 mL sample of sulfuric acid is completely neutralized by adding 32.8 mL of 0.116 mol/L ammonia solution. Ammonium sulfate, (NH₄)₂SO₄, and water are formed. What is the concentration of the sulfuric acid?
- 🟮 💶 The following data were collected during a titration. Calculate the concentration of the sodium hydroxide solution.

Titration Data

| Volume of HCl _(eq) | 10.00 mL |
|--|-------------|
| Final volume of NaOH _(aq) | 23.08 mL |
| Initial volume of NaOH _(aq) | 1.06 mL |
| Concentration of HCI _(aq) | 0.235 mol/L |

- 6 D You should always put the two solutions for a titration experiment in clean, dry beakers. You do not need to dry the Erlenmeyer flask to which you add the solutions, however, if it has been thoroughly rinsed with distilled water. Explain the difference in these procedures.
- 1 Guppose that a laboratory technician accidentally spills a dilute solution of a strong acid on her hands, the sleeve of her lab coat, and the laboratory bench. Explain how she would deal with this spill.

CHAPTER 10 Review

Reflecting on Chapter 10

Summarize this chapter in the format of your choice. Here are a few ideas to use as guidelines:

- Compare the properties of acids and bases.
- · Distinguish the two theories for explaining the behaviour and composition of acids and bases.
- · Identify conjugate acid-base pairs for selected acid-base reactions.
- · Describe strong and weak acids and bases on the basis of their dissociation.
- Explain the significance of the concentration of hydronium ion in describing pH.
- Dilute an acid and describe the effect on its pH.
- Describe and conduct a titration procedure.

Reviewing Key Terms

For each of the following terms, write a sentence that shows your understanding of its meaning.

Arrhenius theory hydronium ion Brønsted-Lowry theory conjugate acid-base pair pH conjugate base conjugate acid strong acid weak acid

strong base

weak base binary acid oxoacid

neutralization reaction salt

acid-base indicator

titration

equivalence point

end-point

Knowledge/Understanding

- 1. Use the Arrhenius theory and then the Brønsted-Lowry theory to describe the following concepts. If one of the theories does not apply, state that this is the case.
 - (a) composition of an acid and a base
 - (b) conductivity of an acidic or basic solution
 - (c) interaction between an acid and water
 - (d) interaction between a base and water
 - (e) conjugate acid-base pairs
 - (f) strong and weak acids and bases
 - (g) the pH of a solution
- 2. How does diluting an acidic or basic solution affect the pH of the solution?
- 3. Codeine is a compound that is extracted from opium. It is used for pain relief. The pH of a 0.020 mol/L solution of codeine is 10.26. Is codeine an acid or a base? Is it strong or weak? Explain how you decided.

- Sodium hydrogen carbonate, NaHCO₃ (commonly called sodium bicarbonate, or bicarbonate of soda), is commonly used in baked goods. It dissolves in water to form an alkaline solution.
 - (a) Is the pH of NaHCO3(aq) greater or less than 7.00?
 - (b) Write the name and formula of an acid and a base that react together to form this compound. Identify each as strong or weak.
- 5. Aluminum sulfate, Al₂(SO₄)₃, is used to help clarify water. In aqueous solution, it is slightly acidic.
 - (a) Is the pH of Al₂(SO₄)_{3(au)} greater or less than 7.00?
 - (b) Write the name and formula of an acid and a base that react together to form aluminum sulfate. Identify each as either strong
- 6. Sodium hydrogen carbonate can be used to neutralize an acid. The hydrogen carbonate ion is the conjugate base of which acid?
- 7. Write the net ionic equation for the reaction of aqueous sodium hydroxide with aqueous nitric acid.
- 8. In different reactions in aqueous solution, the hydrogen carbonate ion can act as an acid or a base. Write the chemical formula of the conjugate acid and the conjugate base of the hydrogen carbonate ion, HCO3-[aq]. Then complete the following equations. State whether the ion is a Brønsted-Lowry acid or a base.
 - (a) $HCO_3^-(aq) + H_3O^+(aq) \rightarrow$
 - (b) $HCO_3^-(aq) + OH^-(aq) \rightarrow$
- 9. Which of the following are conjugate acid-base pairs? For those pairs that are not conjugates, write the correct conjugate acid or base for each compound or ion.
 - (a) HNO₃/OH-
- (c) HSO₄-/SO₄²-
- (b) NH₄+/NH₃
- (d) H₃PO₄/PO₄³⁻
- 10. In the laboratory, you have samples of three different acids of equal concentration: a 1.0 mol/L solution of acetic acid, a 1.0 mol/L solution of hydrochloric acid, and a 1.0 mol/L solution of sulfuric acid.
 - (a) How would the pH of each acid solution compare? Explain.

- (b) If samples of each acid were used in separate titration experiments with 0.50 mol/L sodium hydroxide solution, how would the volume of acid required for neutralization compare? State your reasoning.
- 11. Write balanced chemical equations for the following reactions:
 - (a) calcium oxide with hydrochloric acid
 - (b) magnesium with sulfuric acid
 - (c) sodium carbonate with nitric acid
- 12. Domestic bleach is typically a 5% solution of sodium hypochlorite, NaOCl_(aq). It is made by bubbling chlorine gas through a solution of sodium hydroxide.
 - (a) Write a balanced chemical equation showing the reaction that takes place.
 - (b) In aqueous solution, the hypochlorite ion combines with H⁺_(aq) present in water to form hypochlorous acid. Write the equation for this reaction. Is the hypochlorite ion acting as an acid or a base?
- 13. In this chapter, you are told that $[H_3O^+]$ in pure water is 1.0×10^{-7} mol/L at 25°C. Thus, two out of every one billion water molecules have dissociated. Check these data by answering the following questions.
 - (a) What is the mass (in g) of 1.0 L of water?
 - (b) Calculate the amount (in mol) of water in 1.0 L. This is the concentration of water in mol/L.
 - (c) Divide the concentration of hydronium ions by the concentration of water. Your answer should be about 2 ppb.

Inquiry

- 14. 80.0 mL of 4.00 mol/L, H_2SO_4 are diluted to 400.0 mL by adding water. What is the molar concentration of the sulfuric acid after dilution?
- 15. In a titration experiment, 25.0 mL of an aqueous solution of sodium hydroxide was required to neutralize 50.0 mL of 0.010 mol/L hydrochloric acid. What is the molar concentration of the sodium bydroxide solution?
- 16. A burette delivers 20 drops of solution per 1.0 mL. What amount (mol) of H⁺_(aq) is present in one drop of a 0.20 mol/L HCl solution?

17. How is a 1.0 mol/L solution of hydrochloric acid different from a 1.0 mol/L solution of acetic acid? Suppose that you added a strip of magnesium metal to each acid. Would you observe any differences in the reactions? Explain your answer so that grade 9 students could understand it.

Communication

- 18. Commercial processors of potatoes remove the skin by using a 10-20% by mass solution of sodium hydroxide. The potatoes are snaked in the solution for a few minutes at 60-70°C, after which the peel can be sprayed off using fresh water. You work in the laboratory at a large food processor and must analyse a batch of sodium hydroxide solution. You pipette 25.00 mL of NaOH_(aq), and find it has a mass of 25.75 g. Then you titrate the basic solution against 1.986 mol/L HCI, and find it requires 30.21 mL of acid to reach an end point.
 - (a) Inform your supervisor what the molar concentration of the sodium hydroxide is.
 - (b) The mass percent of NaOH present must be a minimum of 10% for the solution to be used. Advise your supervisor whether or not the solution can be used to process more potatoes, and explain your reasoning.
- 19. Ammonia is an important base, used to make fertilizers, nylon, and nitric acid. The manufacture of ammonia depends on a process discovered by Fritz Haber (1868-1934). After gathering information from print or electronic resources, write an obituary for Haber. Describe his accomplishments and the effect on society of plentiful supplies of ammonia.

Making Connections

20. Limestone, chalk, and marble are all forms of calcium carbonate. Limestone rock can be used to build roads, but it is a very important basic compound used in large quantities by chemical industries. For example, limestone is used directly to make concrete and cement. It is also used in the manufacture of glass and in agriculture. Limestone is often processed to make quicklime, CaO, and hydrated lime (calcium hydroxide), Ca(OH)₂.

- (a) Research the uses of quicklime and hydrated lime. Investigate one of these uses further.
- (b) Design a poster illustrating the use you decided to research. Your poster should be both informative and visually interesting. Include a bibliography showing the resources you found useful.
- 21. On several occasions during the past few years, you have studied the environmental issue of acid rain. Now that you have further developed your understanding of acids and bases in this chapter, reflect on your earlier understandings.
 - (a) List two facts about acid rain that you now understand in a more comprehensive way. Explain what is different between your previous and your current understanding in each case.
 - (b) Identify three questions that your teacher could assign as a research project on acid rain. The emphasis of the research must be on how an understanding of chemistry can contribute clarifying the questions and possible solutions involved in this issue. Develop a rubric that would be used to assess any student who is assigned this research project.
- 22. Research the use of hypochlorous acid in the management of swimming pools and write a report on your findings. Include a discussion on the importance of controlling pool water.

Answers to Practice Problems and Short Answers to Section Review Questions

Practice Problems: 1. HCN/CN- and H2O/H3O+ 2. H2O/OH- and CH3COO-/CH3COOH 3. as an acid:

 $HS^{-}_{(aq)} + H_2O_{(\ell)} \leftrightarrow S^{2-}_{(aq)} + H_3O^{+}_{(aq)}$; as a base:

 $HS^-_{(aq)} + H_2O_{(\ell)} \leftrightarrow H_2S_{(aq)} + OH^-_{(aq)}$ 4.(a) HBr; bromate; Br (b) hydrogen sulfide, HS; sulfide, S2 5.(a) nitric acid, HNO3; nitrate, NO3 (b) nitrous acid, HNO2; nitrite, NO2 (c) hyponitrous acid, HNO; hyponitrite, NO- (d) phosphoric acid, H3PO4; dihydrogen phosphate, H2PO4", hydrogen phosphate, HPO42-, phosphate, PO43- (e) phosphorous acid, H3PO3; dihydrogen phosphite, $H_2PO_3^-$, hydrogen phosphite, HPO_3^{2-} , phosphite, PO₃3- (f) periodic acid, HlO₄; periodate, IO₄- 6.(a) 2.57 (b) 7.138 (c) 4.01 (d) 11.082 7. pH = 2.30; acidic 8, 3.54; acidic 9.(a) 2.20 (b) 9.181; basic 10. 0.210 mol/L 11. 31.5 mL 12.(a) 22.5 mL (b) 24.7 mL (c) 4.8 mL 13.(a) 0.0992 mol/L (b) 0.269 mol/L (c) 0.552 mol/L

Section Review: 10.1: 1.(a) B and D (b) A (C, although unintended, would also be correct) (c) A, B, D (d) no (e) litmus test, for example 5.(a) H₂O (b) HCO₃ 6.(a) NO₃ (b) SO₄² 7. c and d

8. a and b 9.(a) $HF_{(aq)} + H_2O_{(1)} \rightarrow H_3O^*_{(aq)} + F^*_{(aq)}$ (b) $HF/F^*_{;}$ H₂O/H₃O+ 10.(a) H₂PO₄-/HPO₄²⁻ and CO₃²⁻/HCO₃ (b) HCOOH/HCOO- and CN-/HCN (c) H2PO4-/HPO42- and OH-/H2O 10.2: 3. weak 4. potassium permanganate; permanganic acid, HMnO₄ 5.(a) sulfuric acid, H₂SO₄ (b) hydrofluoric acid, HF (c) hydrosulfuric acid, H₂S (d) bromous acid, HBr₂ 7. egg white, camembert cheese, beets, yogurt, sauerkraut 8.(a) 7.4 (b) 1.4 9.2.90 10.1.0 mol/L; concentrations greater than this give negative pH values, but this gives no advantage over the actual concentration of H₃O+ 10.3: 1. acid + base = salt + water 4. 0.304 mol/L 5. 0.107 mol/L

UNIT 3 An Issue to Analyze

Island at Risk: A Simulation

Background

Would you rather have fish—or chips? People on Prince Edward Island are discovering that their sources of both of these food items are increasingly at risk.

The fertile red soil of Prince Edward Island is famous for potato growing. Agricultural corporations have been increasing their potato plantings on this island province. In the process, they have been eliminating other crops, which has led to a monoculture. ("Monoculture" refers to the growing of a single crop in an area.) Potato pests are posing a huge threat to this profitable cash crop, however. Part of the problem results from the fact that the potato fields are very close together. To combat the pests-potato bugs, in particular-farmers are applying more and more pesticides, fertilizers, and herbicides to the potato fields.



What are the environmental effects of this heavy use of pesticides (insecticides and herbicides)? After heavy rains on the island, large numbers of dead fish have been found in the ocean, and washed up on the shore near the potato farms. The suspected cause is the leaching of sodium arsenite and other pesticides used in the potato fields. Sodium arsenate is a chemical used to kill both weeds and insects. If the poisoning of the ocean waters continues, Prince Edward Island's unique seafood industry will come to an end.





Suggestions for dealing with this problem have included:

- · examples of household chemical products and their uses
- creating a mandatory untilled area spanning 20 m next to waterways;
- growing genetically engineered potatoes that are more blight-resistant. These genetically modified potatoes would contain genes from bacteria that have insecticidal properties;
- employing alternative fertilization and pesticide methods to reduce the amount of chemicals used on the potato crop; and
- rotating crops (that is, alternating types of crops from year to year) so that the spread of potato bugs and the overuse of soil would be less of a problem.

Plan and Present

- 1 Look up the properties of sodium arsenate in either the CRC Handbook or the Merck Manual. As well, search the Internet for an MSDS sheet about sodium arsenate.
- Using your knowledge of solutions and dissolving, explain how the chemicals from the potato fields end up in the water with the fish. Make a diagram. a poster, or a PowerPoint™ presentation that clearly illustrates the processes involved in this type of aquatic pollution.
- 3 Provide a minimum of two advantages and two disadvantages of each of the four possible solutions to the problem.
- 4 The provincial government in Charlottetown has decided that action must be taken, in some form or another. The following people and organizations have been invited to participate on a board to develop an action plan:

Assessment

- After you analyze this issue.
- Assess the quality and practicality of your solution.
- Assess your solution based on how clearly the chemistry concepts are expressed and communicated.
- 2 From what you learned in Unit 3 about solutions and water treatment, do you think there could be other chemical-based solutions to this problem in the future? Give a chemical explanation of how the leachates might be contained, if such processing were possible.
- Try to suggest some safe, alternative methods of reducing weeds, insects, and harmful microorganisms. For example, could boiling water be used as an effective herbicide? Would this method of reducing weeds cause more problems than it would solve? Why or why not?

- · the P. E. I. Potato Board
- · the scientists who helped develop the genetically engineered, blight-resistant potato variety
- · the corporations who want to buy the potatoes and process them
- · people who fish for their living
- · potato farmers
- (a) Your class will be divided into groups, and each group will research the point of view of one of these interest groups. Consider questions such as these:
 - · To what extent do landowners have the right to determine how they use their land?
 - · What recourse should the fishers on P.E.I. have available to them to respond to the threat posed to their livelihood?
 - · What possible consumers' rights need to be assessed in analyzing this issue?
- (b) Before developing an action plan, each group should decide on and state clearly their motive and their mandate. In other words, what is the reason for their existence as a group and to whom is the group accountable? For example:
 - Are the scientists working for biotechnology companies or are they doing pure research?
 - What is each group's present policy regarding issues such as environmental protection and sustainability?
 - What points might be included in each group's short-term and long-term action plan?
- (c) Make a one-page summary of your points to hand out to other members at the meeting. A large diagram, poster, overhead transparency, or PowerPoint" slide will help your group illustrate how your action plan:
 - · will affect the environment
 - acknowledges the scientific realities of the leaching situation
 - · satisfies the needs of other interest groups
- (d) Hold a meeting of the action plan board, to present all points of view, and to try to reach a consensus on an action plan.

Evaluate the Results

- 1) (a) Take notes on every point of view presented during the meeting.
 - (b) Decide what you think the best solution is, for everyone involved. Why do you consider it to be the best solution?

Web

LINK

www.school.mcgrawhill.ca/resources/ Go to McGraw-Hill Ryerson's Chemistry 11 web site at the above address, and then follow the links to access further information.

Review

Knowledge/Understanding

True/False

In your notebook, indicate whether each statement is true or false. Correct each false statement.

- 1. The solubility of a gas increases with increased temperature.
- Molar concentration refers to the amount, in moles, of solute dissolved in one kilogram of solvent.
- The maximum amount of a solute that will dissolve in a solvent at a certain temperature is called its solubility.
- 4. The term insoluble has a precise meaning.
- 5. The component of a solution present in the smaller amount is called the solvent.
- The molar concentration of a solution containing 4 mol of solute dissolved in 2 L of solvent is 2 mol/L.
- 7. The rate at which a solid solute dissolves in water can usually be increased by increasing the temperature of the solution.
- 8. Each ten-fold increase in the concentration of hydronium ions in a solution increases the pH of the solution by one unit.
- 9. Hydrobromic acid is a strong acid.

Matching

Match each description in column B with the correct term in column A.

| Column B |
|---|
| A solution with $pH = 10$ |
| NH_3 |
| SO ₃ ²⁻ |
| H_2SO_3 |
| A solution that contains a relatively large amount of solute |
| A solution with $pH = 8$ |
| When solute is added to an aqueous solution, the solute does not dissolve |
| |

- (h) The conjugate base of HSO_3^-
- (i) A solution more acidic than one with pH = 9
- (j) A solution more basic than one with pH = 9

When solute is added to an aqueous solution, the solute dissolves

A substance that produces H+ when dissolved in water

A solution that contains a relatively small amount of solute

Multiple Choice

In your notebook, write the letter of the best answer for each of the following questions.

- 11. Which of the following would best indicate that a sample of water is pure?
 - (a) Measure its boiling point.
 - (b) Measure its pH.
 - (c) Add it to a sample of pure water and see if it is miscible (dissolves infinitely).
 - (d) Pass an electric current through it to see if it decomposes into hydrogen gas and oxygen gas.
 - (e) See if sodium chloride dissolves in it.
- 12. If 1.00 g of solid sodium chloride is dissolved in enough water to make 350 mL of solution, what is the molar concentration of the solution?
 - (a) 5.98 mol/L
 - **(b)** $1.67 \times 10^{-1} \text{ mol/L}$
 - (c) 4.89×10^{-2} mol/L
 - (d) $5.98 \times 10^{-3} \text{ mol/L}$
 - (e) 4.88×10^{-5} mol/L
- 13. What volume of 5.00×10^{-2} mol/L Ca(NO₃)₂ solution will contain 2.50×10^{-2} mol of nitrate ions?
 - (a) 200 mL
 - (b) 250 mL
 - (c) 500 mL
 - (d) 750 mL
 - (e) 1.00 L
- 14. If 40.0 mL of 6.00 mol/L sulfuric acid is diluted to 120 mL by the addition of water, what is the molar concentration of the sulfuric acid after dilution?
 - (a) 5.00×10^{-2} mol/L
 - (b) $7.50 \times 10^{-2} \text{ mol/L}$
 - (c) 1.00 mol/L



- (e) 4.0 mol/L
- 15. When solutions of sodium chloride, NaCl, and silver nitrate, AgNO₃, are mixed, what is the net ionic equation for the reaction that results?
 - (a) $Na^{+}_{(aq)} + NO^{-}_{3(aq)} \rightarrow NaNO_{3(aq)}$
 - (b) $Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)}$
 - (c) $Na^{+}_{(aq)} + NO_{3}^{-}(aq) + Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)} + NaNO_{3(aq)}$
 - (d) $Na^{+}_{(aq)} + NO_{3} {}_{(aq)} + Ag + {}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)} + Na^{+}_{(aq)} + NO_{3[aq)}$
 - (e) $Na^{+}_{(aq)} + NO_{3}^{-}_{(aq)} + Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow NaNO_{3(aq)} + Ag^{+}_{(aq)} + Na^{+}_{(aq)}$
- 16. The acidity in a sample of soil could be neutralized by adding:
 - (a) sodium chloride
 - (b) ammonium nitrate
 - (c) potassium sulfate
 - (d) calcium oxide
 - (e) magnesium phosphate

Short Answers

In your notebook, write a sentence or a short paragraph to answer each of the following questions:

- 17. Is a saturated solution always a concentrated solution? Give an example to explain your answer.
- 18. How can a homogeneous mixture be distinguished from a heterogeneous mixture? Give one example of each.
- 19. List three different ways in which the concentration of a solution could be described.
- 20. What would you observe if a saturated solution of sodium carbonate (commonly called washing soda) at room temperature was cooled to 5°C?
- 21. Explain why calcium hydroxide (solubility 0.165 g per 100 g water at 20°C) is much more soluble than magnesium hydroxide (solubility 0.0009 g per 100 g water at 20°C).
- 22. Iron concentrations of 0.2 to 0.3 parts per million in water can cause fabric staining when washing clothes. A typical wash uses 12 L of water. What is the maximum mass of iron that can be present so that the clothes will not be stained?

- 23. High levels of phosphorus are not toxic, but can cause digestive problems. The allowable drinking water concentration is 0.05 ppm. What is the maximum mass of phosphorus that could be present in a 250 mL glass of tap water?
- 24. Is a 1% solution of table salt, $NaCl_{(aq)}$, more concentrated, less concentrated, or at the same concentration as a 1% solution of sugar, $C_{12}H_{22}O_{11(aq)}$? Explain.
- 25. Bones and teeth consist mostly of a compound called hydroxyapatite, Ca₁₀(PO₄)₆(OH)₂. This compound contains PO₄³⁻ and OH⁻ ions.
 - (a) Do you expect hydroxyapatite will be an acid or a base?
 - (b) Foods that contain sucrose form lactic acid in the mouth and the pH drops. As a result, eating candy promotes a reaction between hydroxyapatite and H⁺_(aq). Balance the skeleton reaction: Ca₁₀(PO₄)₆(OH)₂ + H⁺_(aq) → CaHPO_{4(s)} + H₂O_(ℓ) + Ca²⁺_(aq)
 - (c) At lower pH values, the CaHPO_{4(s)} also reacts with H⁺_(aq): CaHPO_{4(s)} + H⁺_(aq) → Ca²⁺_(aq) + H₂PO₄⁻_(aq) Dentists and toothpaste manufacturers warn that eating candy promotes tooth decay. What chemical evidence have you seen to support this advice?
- **26.** (a) Why does water from different regions vary in its hardness?
 - (b) Why is filtration not an effective method to remove the hardness from water?
 - (c) Why should hard water be treated before it is heated in a hot water boiler?
- 27. Vinegar is added to a kettle with a build-up of scale due to hard water. What would you expect to observe? Explain.
- 28. Chloroform and diethyl ether were among the first substances used as anaesthetics. Both are non-polar substances.
 - (a) Would you expect either or both of these substances to be soluble in water? Explain.
 - (b) Write a sentence or two to describe how you think these substances are able to get from the lungs to the brain.

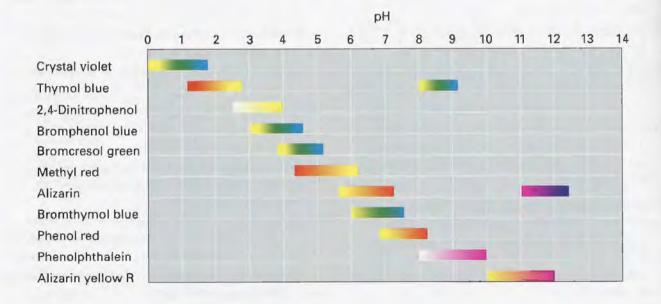
Inquiry

- 29. A Chemist has a large beaker containing ice-cold water, and another containing boiling water. The laboratory is well-equipped with other apparatus.
 - (a) Explain how the chemist could maximize the solubility of the following solutes in water (following appropriate safety precautions):
 - (i) magnesium chloride, MgCl2, used to fireproof wood
 - (ii) benzene, a non-polar liquid used by the industry and found in gasoline
 - (iii) carbon monoxide, CO, a poisonous gas formed by incomplete combustion of hydrocarbons
 - (b) Explain how you could minimize the solubility of the same solutes in water.
- 30. Design an experiment to collect data on the pH of a stream, over a period of one year. Why might the pH vary at different times of the year?
- 31. The table below shows the colours of various indicators at different pH values.
 - (a) If a vinegar solution is at pH 5, what colour would you expect the following indicators to show if placed into separate samples of the vinegar?
 - (i) Thymol blue

- (ii) Bromophenol blue
- (iii) Phenolphthalein
- (b) An aqueous solution of sodium acetate used in photographic development makes phenol red indicator red, and phenolphthalein pink. What is the pH of this sodium acetate solution?

Communicating

- 32. Lead is highly toxic when absorbed into the body, especially for young children. A level of 10 micrograms of lead per decilitre of blood is cause for concern. Do research, then write a report describing the health effects of lead. Include information on the sources of this heavy metal and on how lead might be absorbed by a child.
- 33. Sulfuric acid is the chemical produced in the largest quantity in the world. Research some of the uses of sulfuric acid. Design a poster for students in a younger grade, illustrating one way in which this acid is used. Your poster should be informative and visually interesting.
- 34. In the past, scurvy was a disease that killed many sailors. James Lind discovered that eating citrus fruits prevents scurvy. Citrus fruits contain ascorbic acid (vitamin C). Research the life of James Lind, and write a brief biography.



Making Connections

- 35. The disposal of nuclear waste presents many difficulties. Some proposals suggest burying the waste in glass or ceramic containers deep in the earth.
 - (a) Why would these containers be superior to containers made of metal or concrete?
 - (b) What are some of the concerns related to burying radioactive waste?
 - (c) Make a suggestion on a different way to dispose of radioactive waste. Include a list of the pros and cons of your suggestion.
- 36. The following is a short list of some weak bases and their uses. Which ones are Brønsted–Lowry bases, but not Arrhenius bases?
 - (a) ammonia, NH₃, used in the manufacture of fertilizers, plastics, and explosives
 - (b) zinc oxide, ZnO, a white pigment used in paints and cosmetics
 - (c) copper(II) hydroxide, Cu(OH)₂, used to kill fungi and bacteria
 - (d) hydrazine, N₂H₄, a colourless liquid that can be used as a rocket fuel
- 37. In 1963, a treaty was signed by the US, UK, and USSR to ban the atmospheric testing of atomic weapons. Previous testing of atomic weapons had added radioactive isotopes of strontium (Sr-90) and cesium (Cs-137) to the atmosphere. Eventually, these pollutants fell to the ground and may have entered the food chain.
 - (a) Which would you expect to form more soluble compounds, strontium or cesium? Explain your answer.
 - (b) State two important factors that might help you to determine the health risks of these isotopes.

COURSE CHALLENG



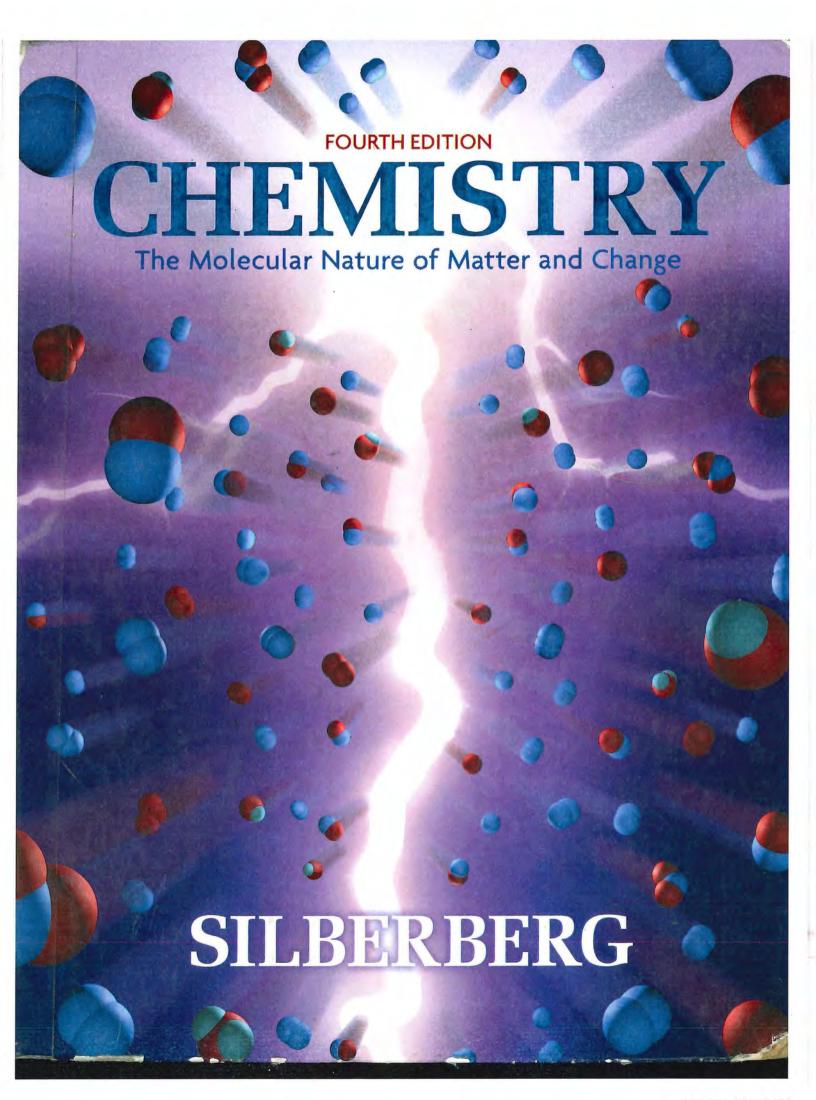
Think about these questions as you plan for your Chemistry Course Challenge.

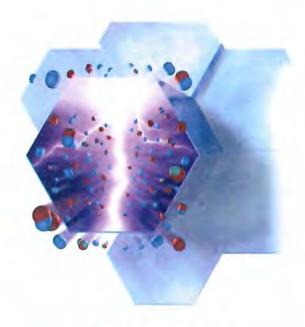
- How might you use your knowledge of solutions to analyze the purity of a sample of water?
- How could you precipitate out contaminants to purify a sample of water?
- What dissolved substances might end up in water as it passes through rock? How might you identify these substances? How could you extract them from the contaminated water?



EXHIBIT D

Previously Filed as ECF No. 63, Exhibit 10





FOURTH EDITION

CHEMISTRY

The Molecular Nature of Matter and Change

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CHEMISTRY: THE MOLECULAR NATURE OF MATTER AND CHANGE, FOURTH EDITION

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1 2 3 4 5 6 7 8 9 0 DOW/DOW 0 9 8 7 6 5 4 1 2 3 4 5 6 7 8 9 0 DOW/DOW 0 9 8 7 6 5 4

ISBN 0-07-255820-2

ISBN 0-07-296439-1 (Annotated Instructor's Edition)

Editorial Director: Kent A. Peterson Sponsoring Editor; Thomas D. Timp

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Supplement Producer: Brenda A. Ernzen

Compositor: The GTS Companies/Los Angeles, CA Campus

Typeface: 10.5/12 Times Roman Printer: R. R. Donnelley, Willard, OH

The credits section for this book begins on page C-1 and is considered an extension of the copyright page.

Library of Congress Cataloging-in-Publication Data

Silberberg, Martin S. (Martin Stuart), 1945-

Chemistry: the molecular nature of matter and change / Martin S. Silberberg. - 4th ed.

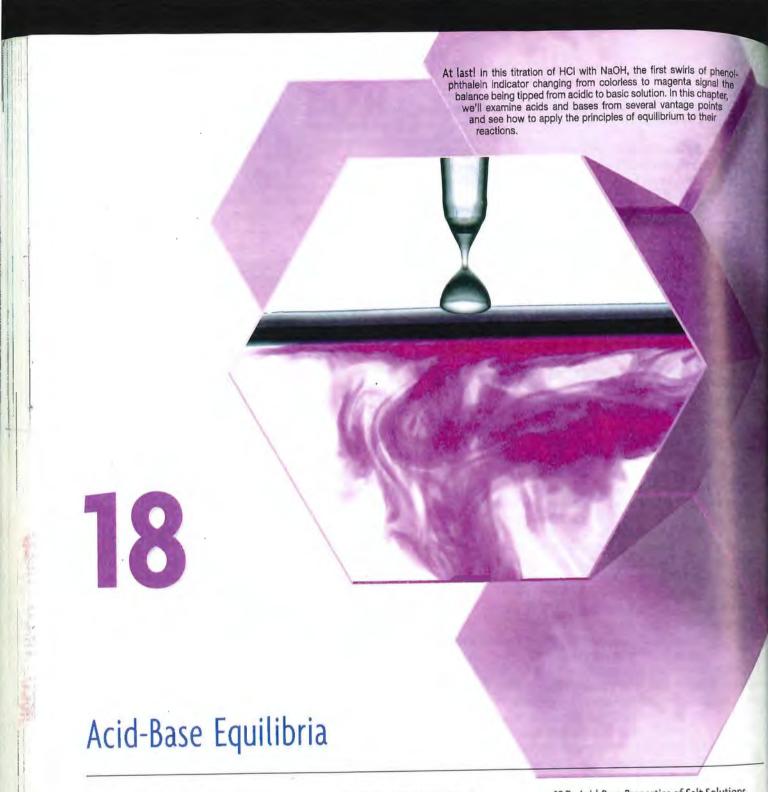
p. cm.
 Includes bibliographical references and index.
 ISBN 0-07-255820-2 (hard copy: alk, paper)

1. Chemistry. I. Title.

QD33.2.S55 2006 540—dc22

2004018874 CIP

www.mhhe.com



- 18.1 Acids and Bases in Water
 The Classical Acid-Base Definition
 The Acid-Dissociation Constant (K_a)
 Relative Strengths of Acids and Bases
- 18.2 Autoionization of Water and the pH Scale Autoionization and $K_{\rm W}$ The pH Scale
- 18.3 Proton Transfer and the Brønsted-Lowry Acid-Base Definition The Conjugate Acid-Base Pair Net Direction of Acid-Base Reactions
- 18.4 Solving Problems Involving Weak-Acid Equilibria Finding K_a Given Concentrations

- Finding Concentrations Given $K_{\rm a}$ Extent of Acid Dissociation Polyprotic Acids
- 18.5 Weak Bases and Their Relation to Weak Acids
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 The Relation Between K_a and K_b
- 18.6 Molecular Properties and Acid Strength Nonmetal Hydrides Oxoacids Acidity of Hydrated Metal lons
- 18.7 Acid-Base Properties of Salt Solutions
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 Salts That Yield Basic Solutions
 Salts of Weakly Acidic Cations and Weakly
 Basic Anions
- 18.8 Generalizing the Brønsted-Lowry Concept: The Leveling Effect
- 18.9 Electron-Pair Donation and the Lewis Acid-Base Definition Molecules as Lewis Acids Metal Cations as Lewis Acids Overview of Acid-Base Definitions

A cids and bases have been used as laboratory chemicals since the time of the alchemists, and they remain indispensable, not only in academic and industrial labs, but in the home as well (Table 18.1).

Notice that some of the acids (e.g., acetic and citric) have a sour taste. In fact, sourness had been a defining property since the 17th century: an acid was any substance that had a sour taste; reacted with active metals, such as aluminum and zinc, to produce hydrogen gas; and tumed certain organic compounds characteristic colors. (We discuss indicators later and in Chapter 19.) A base was any substance that had a bitter taste and slippery feel and turned the same organic compounds different characteristic colors. (Please remember NEVER to taste or touch laboratory chemicals; instead, try some acetic acid in the form of vinegar on your next salad.) Moreover, it was known that when acids and bases react, each cancels the properties of the other in a process called neutralization. But definitions in science evolve because, as descriptions become too limited, they must be replaced by broader ones. Although the early definitions of acids and bases described distinctive properties, they inevitably gave way to definitions based on molecular behavior.

IN THIS CHAPTER... We develop three definitions of acids and bases that allow us to understand ever-increasing numbers of reactions. In the process, we apply the principles of chemical equilibrium to this essential group of substances. After presenting the classical (Arrhenius) acid-base definition, we examine acid dissociation to see why acids vary in strength. The pH scale is introduced as a means of comparing the acidity or basicity of aqueous solutions. Then, we'll see that the Brønsted-Lowry acid-base definition greatly expands the meaning of "base," along with the scope of chemical changes considered acid-base reactions. We explore the molecular structures of acids and bases to rationalize variations in their strengths and see that the very designations "acid" and "base" depend on relative strengths and on the solvent. Finally, we'll see that the Lewis acid-base definition expands the meaning of "acid" and acid-base behavior even further.

Concepts & Skills to Review

before you study this chapter

- role of water as solvent (Section 4.1)
- writing ionic equations (Section 4.2)
- acids, bases, and acid-base reactions (Section 4.4)
- proton transfer in acid-base reactions (Section 4.4)
- properties of an equilibrium constant (Section 17.2)
- solving equilibrium problems (Section 17.5)

Table 18.1 Some Common Acids and Bases and Their Household Uses

Substance

parance

Acids

Acetic acid, CH₃COOH Citric acid, H₃C₆H₅O₇ Phosphoric acid, H₃PO₄ Boric acid, H₃BO₃ Aluminum salts, NaAl(SO₄)₂·12H₂O Hydrochloric acid (muriatic acid), HCl

Hen

Flavoring, preservative
Flavoring
Rust remover
Mild antiseptic, insecticide
In baking powder, with sodium
hydrogen carbonate
Brick and ceramic tile cleaner



Racos

Sodium hydroxide (lye), NaOH Ammonia, NH₃ Sodium carbonate, Na₂CO₃ Sodium hydrogen carbonate, NaHCO₃

Sodium phosphate, Na₃PO₄ Oven and drain cleaners

Household cleaner
Water softener, grease remover
Fire extinguisher, rising agent in
cake mixes (baking soda),
mild antacid
Cleaner for surfaces before

painting or wallpapering



Pioneers of Acid-Base Chemistry Three 17th-century chemists laid the foundations of acid-base chemistry. Johann Glauber (1604-1668) became renowned for his ability to prepare acids and their salts. Glauber's salt (Na2SO4·10H2O) is still used today for preparing dyes and printing textiles. Otto Tachenius (c. 1620-1690) is credited with first recognizing that a salt is the product of the reaction between an acid and a base. Robert Boyle (1627-1691), in addition to studying gas behavior, fostered the use of spot tests, flame colors, fume odors, and precipitates to analyze reactions. He was the first to associate the color change in syrup of violets (an organic dye) with the acidic or basic nature of the test solution.

Chapter 18 Acid-Base Equilibria

18.1 ACIDS AND BASES IN WATER

Although water is not an essential participant in all modern acid-base definitions, most laboratory work with acids and bases involves water, as do most environmental, biological, and industrial applications. Recall from our discussion in Chapter 4 that water is a product in all reactions between strong acids and strong bases:

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H2O(l)$$

Indeed, as the net ionic equation of this reaction shows, water is the product:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

Furthermore, whenever an acid dissociates in water, solvent molecules participate in the reaction:

$$HA(g \text{ or } l) + H_2O(l) \longrightarrow A^-(aq) + H_3O^+(aq)$$

As you saw in that earlier discussion, water surrounds the proton to form H-bonded species with the general formula $H(H_2O)_n^+$. Because the proton is so small, its charge density is very high, so its attraction to water is especially strong. The proton bonds covalently to one of the lone electron pairs of a water molecule's O atom to form a **hydronium ion**, H_3O^+ , which forms H bonds to several other water molecules (see Figure 4.4, p. 139). To emphasize the active role of water and the nature of the proton-water interaction, the hydrated proton is usually shown in the text as $H_3O^+(aq)$, although in some cases this hydrated species is shown more simply as $H^+(aq)$.

Release of H+ or OH and the Classical Acid-Base Definition

The earliest and simplest definition of acids and bases that reflects their molecular nature was suggested by Svante Arrhenius, whose work on the rate constant we encountered in Chapter 16. In the classical (or Arrhenius) acid-base definition, acids and bases are classified in terms of their formulas and their behavior in water:

- An acid is a substance that has H in its formula and dissociates in water to yield H₃O⁺.
- A base is a substance that has OH in its formula and dissociates in water to yield OH.

Some typical Arrhenius acids are HCl, HNO₃, and HCN, and some typical bases are NaOH, KOH, and Ba(OH)₂. Although Arrhenius bases contain discrete OH⁻ ions in their structures, Arrhenius acids *never* contain H⁺ ions. On the contrary, these acids contain *covalently bonded H atoms that ionize in water*.

When an acid and a base react, they undergo **neutralization**. The meaning of acid-base reactions has changed along with the definitions of acid and base, but in the Arrhenius sense, neutralization occurs when the H^+ ion from the acid and the OH^- ion from the base combine to form H_2O . This description explains an observation that puzzled many of Arrhenius's colleagues. They observed that all neutralization reactions between what we now call strong acids and strong bases (those that dissociate completely in water) had the same heat of reaction. No matter which strong acid and base reacted, and no matter which salt formed, $\Delta H^0_{\rm rxn}$ was about -56 kJ per mole of water formed. Arrhenius suggested that the heat of reaction was always the same because the actual reaction was always the same—a hydrogen ion and a hydroxide ion formed water:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$
 $\Delta H^0_{exp} = -55.9 \text{ kJ}$

The dissolved salt that formed along with the water, for example, NaCl in the reaction of sodium hydroxide with hydrochloric acid,

$$Na^{+}(aq) + OH^{-}(aq) + H^{+}(aq) + CI^{-}(aq) \longrightarrow Na^{+}(aq) + CI^{-}(aq) + H_{2}O(l)$$

did not affect the $\Delta H^0_{\rm rxn}$ but existed as hydrated spectator ions. Despite its importance at the time, limitations in the classical definition soon became apparent. Arrhenius and many others realized that even though some substances do *not* have OH in their formulas, they still behave as bases. For example, NH₃ and K₂CO₃ also yield OH⁻ in water. As you'll see shortly, broader acid-base definitions are required to include these species.

Variation in Acid Strength: The Acid-Dissociation Constant (Ka)

Acids and bases differ greatly in their *strength* in water, that is, in the amount of H_3O^+ or OH^- produced per mole of substance dissolved. We generally classify acids and bases as either strong or weak, according to the extent of their dissociation into ions in water (see Table 4.2, p. 144). Remember, however, that a *gradation* in strength exists, as we'll examine quantitatively in a moment. Acids and bases are electrolytes in water, so this classification of acid and base strength correlates with our earlier classification of electrolyte strength: *strong electrolytes dissociate completely, and weak electrolytes dissociate partially.*

• Strong acids dissociate completely into ions in water (Figure 18.1):

$$HA(g \text{ or } l) + H_2O(l) \longrightarrow H_3O^+(aq) + A^-(aq)$$

In a dilute solution of a strong acid, virtually no HA molecules are present; that is, $[H_3O^+] \approx [HA]_{init}$. In other words, $[HA]_{eq} \approx 0$, so the value of K_c is extremely large:

$$Q_{c} = \frac{[H_{3}O^{+}][A^{-}]}{[HA][H_{2}O]}$$
 (at equilibrium, $Q_{c} = K_{c} >> 1$)

Because the reaction is essentially complete, it is not very useful to express it as an equilibrium process. In a dilute aqueous nitric acid solution, for example, there are virtually no undissociated nitric acid molecules:

$$HNO_3(l) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

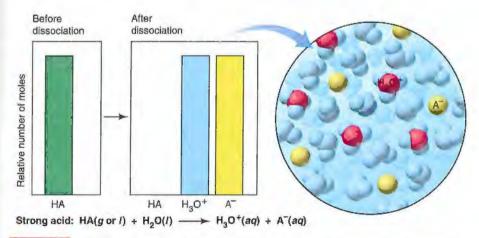


Figure 18.1 The extent of dissociation for strong acids. The bar graphs show the relative numbers of moles of species before (left) and after (right) acid dissociation occurs. When a strong acid dissolves in water, it dissociates completely, yielding H₃O⁺(aq) and A⁻(aq) ions; virtually no HA molecules are present.

Animation: Dissociation of Strong and Weak Acids Online Learning Center

Chapter 18 Acid-Base Equilibria

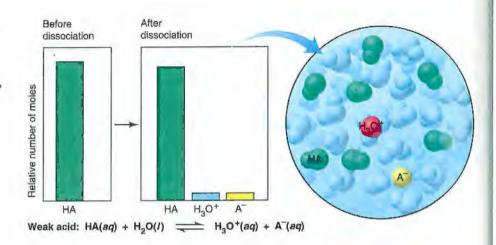
· Weak acids dissociate very slightly into ions in water (Figure 18.2):

$$HA(aq) + H2O(l) \Longrightarrow H3O+(aq) + A-(aq)$$

In a dilute solution of a weak acid, the great majority of HA molecules are undissociated. Thus, $[H_3O^+] << [HA]_{init}$. In other words, $[HA]_{eq} \approx [HA]_{init}$, so the value of K_c is very small. Hydrocyanic acid is an example of a weak acid:

$$\begin{aligned} & \text{HCN}(aq) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CN}^-(aq) \\ & Q_\text{c} = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}][\text{H}_2\text{O}]} & \text{(at equilibrium, } Q_\text{c} = K_\text{c} << 1) \end{aligned}$$

Figure 18.2 The extent of dissociation for weak acids. In contrast to a strong acid in water (see Figure 18.1), a weak acid dissociates very little, remaining mostly as intact acid molecules and, thus, yielding relatively few H₃O⁺(aq) and A⁻(aq) ions.



(From here on, brackets with no subscript mean molar concentration at equilibrium; that is, [X] means $[X]_{eq}$. In this chapter, we are dealing with systems at equilibrium, so instead of writing Q and stating that Q equals K at equilibrium, we'll express K directly as a collection of equilibrium concentration terms.)

Because of the effect of concentration on rate (Section 16.6), this dramatic difference in $[H_3O^+]$ causes a dramatic difference in the reaction rate when an equal concentration of a strong or a weak acid reacts with an active metal, such as zinc (Figure 18.3):

$$Zn(s) + 2H_3O^+(aq) \longrightarrow Zn^{2+}(aq) + 2H_2O(l) + H_2(g)$$

In a strong acid, such as 1 M HCl, zinc reacts rapidly, forming bubbles of H_2 vigorously. In a weak acid, such as 1 M CH₃COOH, zinc reacts slowly, forming bubbles of H_2 sluggishly on the metal piece. The strong acid has a much higher $[H_3O^+]$; much more H_3O^+ ion is available for reaction, so the rate is much higher.

The Meaning of K_a There is a *specific* equilibrium constant for acid dissociation that highlights only those species whose concentrations change to any significant extent. The equilibrium expression for the dissociation of a general weak acid, HA, in water is

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

In general, the concentration of water, $[H_2O]$, is so much larger than [HA] that it changes negligibly when HA dissociates; thus, it is treated as a constant. Therefore, as you saw for solids in Section 17.2, we simplify the equilibrium expression by multiplying $[H_2O]$ by K_c to define a new equilibrium constant, the acid-dissociation constant (or acid-ionization constant), K_a :

$$K_{\rm c}[{\rm H}_2{\rm O}] = K_{\rm a} = \frac{[{\rm H}_3{\rm O}^+][{\rm A}^-]}{[{\rm H}{\rm A}]}$$
 (18.1)



Figure 18.3 Reaction of zinc with a strong and a weak acid. In the reaction of zinc with a strong acid (*left*), the higher concentration of H₃O⁺ results in rapid formation of H₂ (bubbles). In a weak acid (*right*), the H₃O⁺ concentration is much lower, so formation of H₂ is much slower.

Like any equilibrium constant, K_a is a number whose magnitude is temperature dependent and tells how far to the right the reaction has proceeded to reach equilibrium. Thus, the stronger the acid, the higher the $[H_3O^+]$ at equilibrium, and the larger the K_a :

Stronger acid \Longrightarrow higher $[H_3O^+] \Longrightarrow$ larger K_a

The range of values for the acid-dissociation constants of weak acids extends over many orders of magnitude. Listed below are some benchmark K_a values for typical weak acids to give you a general idea of the fraction of HA molecules that dissociate into ions:

- For a weak acid with a relatively high K_a ($\sim 10^{-2}$), a 1 M solution has $\sim 10\%$ of the HA molecules dissociated. The K_a of chlorous acid (HClO₂) is 1.1×10^{-2} , and 1 M HClO₂ is 10.% dissociated.
- For a weak acid with a moderate K_a ($\sim 10^{-5}$), a 1 M solution has $\sim 0.3\%$ of the HA molecules dissociated. The K_a of acetic acid (CH₃COOH) is 1.8×10^{-5} , and 1 M CH₃COOH is 0.42% dissociated.
- For a weak acid with a relatively low K_a (~10⁻¹⁰), a 1 M solution has ~0.001% of the HA molecules dissociated. The K_a of HCN is 6.2×10^{-10} , and 1 M HCN is 0.0025% dissociated.

Thus, for solutions of the same initial HA concentration, the smaller the K_a , the lower the percent dissociation of HA:

Smaller
$$K_a \Longrightarrow$$
 lower % dissociation of HA \Longrightarrow weaker acid

Table 18.2 lists K_a values in water of some weak *monoprotic* acids, those with one ionizable proton. (A more extensive list appears in Appendix C.) Strong acids are absent because they do not have meaningful K_a values. Note that the ionizable proton in organic acids is attached to oxygen in the —COOH group; the H atoms bonded to C atoms do *not* ionize. (In Section 18.4, we discuss the behavior of polyprotic acids, those with more than one ionizable proton.)

| Mame (Formula) | Lewis Structure* | Ka | |
|---|--------------------------------|-----------------------|---------------|
| Chlorous acid (HClO ₂) | H −Ö,−Ö,=Ö | 1.1×10^{-2} | |
| Nitrous acid (HNO ₂) | H-Ö-N=Ö | 7.1×10^{-4} | 4 |
| Hydrofluoric acid (HF) | H—Ë: | 6.8×10^{-4} | |
| Formic acid (HCOOH) | н—с—ё— Н :0: | 1.8×10 ⁻⁴ | |
| Acetic acid (CH ₃ COOH) | н—с—с—ё— н н :0: | 1.8×10 ⁻⁵ | ACID STRENGTH |
| Propanoic acid (CH ₃ CH ₂ COOH) | H H :0: | 1.3×10 ⁻⁵ | ACID |
| Hypochlorous acid (HClO) | H-Ö-Ğ | 2.9×10 ⁻⁸ | |
| Hydrocyanic acid (HCN) | H-C=N: | 6.2×10^{-10} | |

^{*}Red type indicates the ionizable proton; all atoms have zero formal charge.

Chapter 18 Acid-Base Equilibria

Classifying the Relative Strengths of Acids and Bases

Using a table of acid-dissociation constants is the surest way to quantify relative acid strengths, but you can often classify acids and bases qualitatively as strong or weak just from their formulas:

- Strong acids. Two types of strong acids, with examples that you should memorize, are
 - 1. The hydrohalic acids HCl, HBr, and HI
 - 2. Oxoacids in which the number of O atoms exceeds the number of ionizable protons by two or more, such as HNO_3 , H_2SO_4 , and $HClO_4$; for example, in H_2SO_4 , 4 O's 2 H's = 2
- Weak acids. There are many more weak acids than strong ones. Four types, with examples, are
 - I. The hydrohalic acid HF
 - 2. Those acids in which H is not bonded to O or to halogen, such as HCN and H₂S
 - Oxoacids in which the number of O atoms equals or exceeds by one the number of ionizable protons, such as HClO, HNO₂, and H₃PO₄
 - 4. Carboxylic acids (general formula RCOOH), such as CH₃COOH and C₆H₅COOH
- Strong bases. Water-soluble compounds containing O²⁻ or OH⁻ ions are strong bases. The cations are usually those of the most active metals:
 - 1. M₂O or MOH, where M = Group 1A(1) metal (Li, Na, K, Rb, Cs)
 - MO or M(OH)₂, where M = Group 2A(2) metal (Ca, Sr, Ba)
 [MgO and Mg(OH)₂ are only slightly soluble in water, but the soluble portion dissociates completely.]
- Weak bases. Many compounds with an electron-rich nitrogen atom are weak bases (none are Arrhenius bases). The common structural feature is an N atom that has a lone electron pair (shown here in the formulas):
 - 1. Ammonia (NH₃)
 - Amines (general formula RNH₂, R₂NH, or R₃N), such as CH₃CH₂NH₂, (CH₃)₂NH, (C₃H₇)₃N, and C₅H₅N

SAMPLE PROBLEM 18.1 Classifying Acid and Base Strength from the Chemical Formula

Problem Classify each of the following compounds as a strong acid, weak acid, strong base, or weak base:

- (a) H₂SeO₄ (b) (CH₃)₂CHCOOH
- (c) KOH (d) (CH₃)₂CHNH₂

Plan We examine the formula and classify each acid or base, using the text descriptions. Particular points to note for acids are the numbers of O atoms relative to H atoms and the presence of the —COOH group. For bases, note the nature of the cation or the presence of an N atom that has a lone pair.

Solution (a) Strong acid: H₂SeO₄ is an oxoacid in which the number of O atoms exceeds the number of ionizable protons by two.

- (b) Weak acid: (CH₃)₂CHCOOH is a carboxylic acid, as indicated by the —COOH group.
- (c) Strong base: KOH is one of the Group 1A(1) hydroxides.
- (d) Weak base: (CH₃)₂CHNH₂ has a lone pair on the N and is an amine.

FOLLOW-UP PROBLEM 18.1 Which member of each pair is the stronger acid or base?

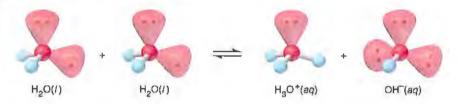
(a) HClO or HClO₃ (b) HCl or CH₃COOH (c) NaOH or CH₃NH₂

SECTION SUMMARY

Acids and bases are essential substances in home, industry, and the environment. In aqueous solution, water combines with the proton released from an acid to form the hydrated species represented by $H_3O^+(aq)$. In the classical (Arrhenius) definition, acids contain H and yield H_3O^+ in water, bases contain OH and yield OH $^-$ in water, and an acid-base reaction (neutralization) is the reaction of H $^+$ and OH $^-$ to form H_2O . Acid strength depends on $[H_3O^+]$ relative to [HA] in aqueous solution. Strong acids dissociate completely and weak acids slightly. The extent of dissociation is expressed by the acid-dissociation constant, K_a . Weak acids have K_a values ranging from about 10^{-1} to 10^{-12} . Acids and bases can be classified qualitatively as strong or weak based on their formulas.

18.2 AUTOIONIZATION OF WATER AND THE pH SCALE

Before we discuss the next major definition of acid-base behavior, let's examine a crucial property of water that enables us to quantify $[H_3O^+]$ in any aqueous system: water is an extremely weak electrolyte. The electrical conductivity of tap water is due almost entirely to dissolved ions, but even water that has been repeatedly distilled and deionized exhibits a tiny conductance. The reason is that water itself dissociates into ions very slightly in an equilibrium process known as autoionization (or self-ionization):



The Equilibrium Nature of Autoionization: The Ion-Product Constant for Water (K_w)

Like any equilibrium process, the autoionization of water is described quantitatively by an equilibrium constant:

$$K_{\rm c} = \frac{[{\rm H_3O}^+][{\rm OH}^-]}{[{\rm H_2O}]^2}$$

Because the concentration of H_2O is essentially constant here, we simplify this equilibrium expression by including the constant $[H_2O]^2$ term with the value of K_c to obtain a new equilibrium constant, the ion-product constant for water, K_w :

$$K_c[H_2O]^2 = K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ (at 25°C)}$$
 (18.2)

Notice that one H_3O^+ ion and one OH^- ion appear for each H_2O molecule that dissociates. Therefore, in pure water, we find that

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} M \text{ (at 25°C)}$$

Pure water has a concentration of about 55.5 M (that is, $\frac{1000 \text{ g/L}}{18.02 \text{ g/mol}}$), so these equilibrium concentrations are attained when only 1 in 555 million water mol-

ecules dissociates reversibly into ions!

Autoionization of water has two major consequences for aqueous acid-base

chemistry: 1. A change in $[H_3O^+]$ causes an inverse change in $[OH^-]$, and vice versa:

Higher
$$[H_3O^+] \Rightarrow lower [OH^-]$$
 and Higher $[OH^-] \Rightarrow lower [H_3O^+]$

Chapter 18 Acid-Base Equilibria

Recall from our discussion of Le Châtelier's principle (Section 17.6) that a change in concentration of either ion shifts the equilibrium position, but it does not change the equilibrium constant. Therefore, if some acid is added, $[H_3O^+]$ increases, and so $[OH^-]$ must decrease; if some base is added, $[OH^-]$ increases, and so $[H_3O^+]$ must decrease. However, the addition of H_3O^+ or OH^- merely leads to the formation of H_2O , so the value of K_w is maintained.

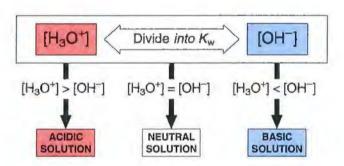
2. Both ions are present in all aqueous systems. Thus, all acidic solutions contain a low concentration of OH^- ions, and all basic solutions contain a low concentration of H_3O^+ ions. The equilibrium nature of autoionization allows us to define "acidic" and "basic" solutions in terms of relative magnitudes of $[H_3O^+]$ and $[OH^-]$:

In an acidic solution, $[H_3O^+] > [OH^-]$ In a neutral solution, $[H_3O^+] = [OH^-]$ In a basic solution, $[H_3O^+] < [OH^-]$

Figure 18.4 summarizes these relationships and the relative solution acidity. Moreover, if you know the value of $K_{\rm w}$ at a particular temperature and the concentration of one of these ions, you can easily calculate the concentration of the other ion by solving for it from the $K_{\rm w}$ expression:

$$[H_3O^+] = \frac{K_w}{[OH^-]}$$
 or $[OH^-] = \frac{K_w}{[H_3O^+]}$

Figure 18.4 The relationship between $[H_3O^+]$ and $[OH^-]$ and the relative acidity of solutions.



SAMPLE PROBLEM 18.2 Calculating [H₃O⁺] and [OH⁻] in Aqueous Solution

Problem A research chemist adds a measured amount of HCl gas to pure water at 25°C and obtains a solution with $[H_3O^+] = 3.0 \times 10^{-4} M$. Calculate $[OH^-]$. Is the solution neutral, acidic, or basic?

Plan We use the known value of K_w at 25°C (1.0×10⁻¹⁴) and the given $[H_3O^+]$ (3.0×10⁻⁴ M) to solve for $[OH^-]$. Then, referring to Figure 18.4, we compare $[H_3O^+]$ with $[OH^-]$ to determine whether the solution is acidic, basic, or neutral. Solution Calculating $[OH^-]$:

$$[OH^{-}] = \frac{K_{\text{w}}}{[H_3O^{+}]} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-4}}$$
$$= 3.3 \times 10^{-11} M$$

Because $[H_3O^+] > [OH^-]$, the solution is acidic.

Check It makes sense that adding an acid to water results in an acidic solution. Moreover, because $[H_3O^+]$ is greater than $10^{-7} M$, $[OH^-]$ must be less than $10^{-7} M$ to give a constant K_w .

FOLLOW-UP PROBLEM 18.2 Calculate $[H_3O^+]$ in a solution that is at 25°C and has $[OH^-] = 6.7 \times 10^{-2} M$. Is the solution neutral, acidic, or basic?

Expressing the Hydronium Ion Concentration: The pH Scale

In aqueous solutions, $[H_3O^+]$ can vary from about 10 M to 10^{-15} M. To handle numbers with negative exponents more conveniently in calculations, we convert them to positive numbers using a numerical system called a *p-scale*, the negative of the common (base-10) logarithm of the number. Applying this numerical system to $[H_3O^+]$ gives **pH**, the negative logarithm of $[H^+]$ (or $[H_3O^+]$):

$$pH = -log [H_3O^+]$$
 (18.3)

What is the pH of $10^{-12} M H_3 O^+$ solution?

$$pH = -log [H_3O^+] = -log 10^{-12} = (-1)(-12) = 12$$

Similarly, a 10^{-3} M H₃O⁺ solution has a pH of 3, and a 5.4×10^{-4} M H₃O⁺ solution has a pH of 3.27:

$$pH = -\log [H_3O^+] = (-1)(\log 5.4 + \log 10^{-4}) = 3.27$$

As with any measurement, the number of significant figures in a pH value reflects the precision with which the concentration is known. However, it is a logarithm, so the number of significant figures in the concentration equals the number of digits to the right of the decimal point in the logarithm (see Appendix A). In the preceding example, $5.4 \times 10^{-4} M$ has two significant figures, so its negative logarithm, 3.27, has two digits to the right of the decimal point.

Note in particular that the higher the pH, the lower the $[H_3O^+]$. Therefore, an acidic solution has a lower pH (higher $[H_3O^+]$) than a basic solution. At 25°C in pure water, $[H_3O^+]$ is 1.0×10^{-7} M, so

Figure 18.5 shows that the pH values of some familiar aqueous solutions fall within a range of 0 to 14.

Another important point arises when we compare $[H_3O^+]$ in different solutions. Because the pH scale is logarithmic, a solution of pH 1.0 has an $[H_3O^+]$ that is 10 times higher than that of a pH 2.0 solution, 100 times higher than that of a pH 3.0 solution, and so forth. To find the $[H_3O^+]$ from the pH, you perform the opposite arithmetic process; that is, you find the negative antilog of pH:

$$[H_3O^+] = 10^{-pH}$$

A p-scale is used to express other quantities as well:

· Hydroxide ion concentration can be expressed as pOH:

$$pOH = -log [OH^-]$$

Acidic solutions have a higher pOH (lower [OH-]) than basic solutions.

· Equilibrium constants can be expressed as pK:

$$pK = -\log K$$

A low pK corresponds to a high K. A reaction that reaches equilibrium with mostly products present (that proceeds far to the right) has a low pK (high K), whereas one that has mostly reactants present at equilibrium has a high pK (low K). Table 18.3 shows this relationship for aqueous equilibria of some weak acids.

| cid Name (Formula) | Ka at 25°C | pK _a |
|---|-----------------------|-----------------|
| Hydrogen sulfate ion (HSO ₄ ⁻) | 1,0×10 ⁻² | 1,99 |
| Nitrous acid (HNO ₂) | 7.1×10^{-4} | 3.15 |
| Acetic acid (CH ₃ COOH) | 1.8×10^{-5} | 4.74 |
| Hypobromous acid (HBrO) | 2.3×10^{-9} | 8.64 |
| Phenol (C ₆ H ₅ OH) | 1.0×10^{-10} | 10.00 |

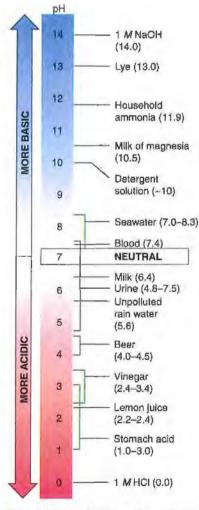


Figure 18.5 The pH values of some familiar aqueous solutions.

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Figure 18.6 The relations among $[H_3O^+]$, pH, $[OH^-]$, and pOH. Because K_w is constant, $[H_3O^+]$ and $[OH^-]$ are interdependent, and they change in opposite directions as the acidity or basicity of the aqueous solution increases. The pH and pOH are interdependent in the same way. Note that at 25°C, the product of $[H_3O^+]$ and $[OH^-]$ is 1.0×10^{-14} , and the sum of pH and pOH is 14.00.

| | | [H ₃ O ⁺] | pН | [OH-] | рОН |
|-------|---------|----------------------------------|-------|-------------------------|-------|
| | 4 | 1.0 x 10 ⁻¹⁵ | 15.00 | 1.0 x 10 ¹ | -1.00 |
| | | 1.0 x 10 ⁻¹⁴ | 14.00 | 1.0 x 10 ⁰ | 0.00 |
| BASIC | | 1.0 x 10 ⁻¹³ | 13.00 | 1.0 x 10 ⁻¹ | 1.00 |
| 8 | BASIC | 1.0 x 10 ⁻¹² | 12.00 | 1.0 x 10 ⁻² | 2.00 |
| MORE | | 1.0 x 10 ⁻¹¹ | 11.00 | 1.0 x 10 ⁻³ | 3.00 |
| ž | | 1.0 x 10 ⁻¹⁰ | 10.00 | 1.0 x 10 ⁻⁴ | 4.00 |
| | | 1.0 x 10 ⁻⁹ | 9.00 | 1.0 x 10 ⁻⁵ | 5.00 |
| | | 1.0 x 10 ⁻⁸ | 8.00 | 1.0 x 10 ⁻⁶ | 6.00 |
| | NEUTRAL | 1.0 x 10 ⁻⁷ | 7.00 | 1.0 x 10 ⁻⁷ | 7.00 |
| | | 1.0 x 10 ⁻⁶ | 6,00 | 1.0 x 10 ⁻⁸ | 8.00 |
| | | 1.0 x 10 ⁻⁵ | 5.00 | 1.0 x 10 ⁻⁹ | 9.00 |
| 음 | | 1.0 x 10 ⁻⁴ | 4.00 | 1.0 x 10 ⁻¹⁰ | 10.00 |
| AC | Aminio | 1.0 x 10 ⁻³ | 3.00 | 1.0 x 10 ⁻¹¹ | 11.00 |
| H. | ACIDIC | 1.0 x 10 ⁻² | 2,00 | 1.0 x 10 ⁻¹² | 12.00 |
| Ş | | 1.0 x 10 ⁻¹ | 1.00 | 1.0 x 10 ⁻¹³ | 13.00 |
| | | 1.0 x 10 ⁰ | 0.00 | 1.0 x 10 ⁻¹⁴ | 14.00 |
| 7 | | 1.0 x 10 ¹ | -1.00 | 1.0 x 10 ⁻¹⁵ | 15.00 |

The Relations Among pH, pOH, and pK_w Taking the negative log of both sides of the K_w expression gives a very useful relationship among pK_w , pH, and pOH:

$$K_{\rm w} = [{\rm H_3O^+}][{\rm OH^-}] = 1.0 \times 10^{-14} \text{ (at 25°C)}$$

 $-\log K_{\rm w} = (-\log [{\rm H_3O^+}]) + (-\log [{\rm OH^-}]) = -\log (1.0 \times 10^{-14})$
 $pK_{\rm w} = p{\rm H} + p{\rm OH} = 14.00 \quad \text{(at 25°C)}$ (18.4)

Thus, the sum of pH and pOH is 14.00 in any aqueous solution at 25°C. With pH, pOH, $[H_3O^+]$, and $[OH^-]$ interrelated through K_w , knowing any one of the values allows us to determine the others (Figure 18.6).

SAMPLE PROBLEM 18.3 Calculating [H3O+], pH, [OH-], and pOH

Problem In an art restoration project, a conservator prepares copper-plate etching solutions by diluting concentrated HNO₃ to 2.0 M, 0.30 M, and 0.0063 M HNO₃. Calculate [H₃O⁺], pH, [OH⁻], and pOH of the three solutions at 25°C.

Plan We know from its formula that HNO₃ is a strong acid, so it dissociates completely; thus, $[H_3O^+] = [HNO_3]_{init}$. We use the given concentrations and the value of K_w at 25°C (1.0×10^{-14}) to find $[H_3O^+]$ and $[OH^-]$ and then use them to calculate pH and pOH. **Solution** Calculating the values for 2.0 M HNO₃:

$$[H_3O^+] = 2.0 M$$

$$pH = -\log [H_3O^+] = -\log 2.0 = -0.30$$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0} = 5.0 \times 10^{-15} M$$

$$pOH = -\log (5.0 \times 10^{-15}) = 14.30$$

Calculating the values for 0.30 M HNO3:

$$[H_3O^+] = 0.30 M$$

$$pH = -\log [H_3O^+] = -\log 0.30 = 0.52$$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{0.30} = 3.3 \times 10^{-14} M$$

$$pOH = -\log (3.3 \times 10^{-14}) = 13.48$$

Calculating the values for 0.0063 M HNO3:

$$[H_3O^+] = 6.3 \times 10^{-3} M$$

 $pH = -log [H_3O^+] = -log (6.3 \times 10^{-3}) = 2.20$
 $[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-3}} = 1.6 \times 10^{-12} M$
 $pOH = -log (1.6 \times 10^{-12}) = 11.80$

Check As the solution becomes more dilute, $[H_3O^+]$ decreases, so pH increases, as we expect. An $[H_3O^+]$ greater than 1.0 M, as in 2.0 M HNO₃, gives a positive log, so it results in a negative pH. The arithmetic seems correct because pH + pOH = 14.00 in each case. **Comment** On most calculators, finding the pH requires several keystrokes. For example, to find the pH of 6.3×10^{-3} M HNO₃ solution, you enter: 6.3, EXP, 3, +/-, log, +/-.

FOLLOW-UP PROBLEM 18.3 A solution of NaOH has a pH of 9.52. What is its pOH, [H₃O⁺], and [OH⁻] at 25°C?

Measuring pH In the laboratory, pH values are usually obtained with an acid-base indicator or, more precisely, with an instrument called a pH meter. Acid-base indicators are organic molecules whose colors depend on the acidity or basicity of the solution in which they are dissolved. The pH of a solution is estimated quickly with pH paper, a paper strip impregnated with one or a mixture of indicators. A drop of test solution is placed on the paper strip, and the color of the strip is compared with a color chart, as shown in Figure 18.7A.

The *pH meter* measures [H₃O⁺] by means of two electrodes immersed in the test solution. One electrode provides a stable reference voltage; the other has an extremely thin, conducting, glass membrane that separates a known internal [H₃O⁺] from the unknown external [H₃O⁺]. The difference in [H₃O⁺] creates a voltage difference across the membrane, which is measured and displayed in pH units (Figure 18.7B). We examine this process further in Chapter 21.

SECTION SUMMARY

Pure water has a low conductivity because it autoionizes to a small extent. This process is described by an equilibrium reaction whose equilibrium constant is the ion-product constant for water, $K_{\rm w}$ (1.0×10⁻¹⁴ at 25°C). Thus, [H₃O⁺] and [OH⁻] are inversely related: in acidic solution, [H₃O⁺] is greater than [OH⁻]; the reverse is true in basic solution; and the two are equal in neutral solution. To express small values of [H₃O⁺] more simply, we use the pH scale (pH = -log [H₃O⁺]). A high pH represents a low [H₃O⁺]. Similarly, pOH = -log [OH⁻], and pK = -log K. In acidic solutions, pH < 7.00; in basic solutions, pH > 7.00; and in neutral solutions, pH = 7.00. The sum of pH and pOH equals pK_w (14.00 at 25°C).

18.3 PROTON TRANSFER AND THE BRØNSTED-LOWRY ACID-BASE DEFINITION

Earlier we noted a major shortcoming of the classical (Arrhenius) definition: many substances that yield OH⁻ ions when they dissolve in water do not contain OH in their formulas. Examples include ammonia, the amines, and many salts of weak acids, such as NaF. Another limitation of the Arrhenius definition was that water had to be the solvent for acid-base reactions. In the early 20th century, J. N. Brønsted and T. M. Lowry suggested definitions that remove these limitations. (Recall that we discussed their ideas briefly in Section 4.4.) According to the Brønsted-Lowry acid-base definition,

An acid is a proton donor, any species that donates an H⁺ ion. An acid must contain H in its formula; HNO₃ and H₂PO₄⁻ are two of many examples. All Arrhenius acids are Brønsted-Lowry acids.





Figure 18.7 Methods for measuring the pH of an aqueous solution. A, A few drops of the solution are placed on a strip of pH paper, and the color is compared with the color chart. B, The electrodes of a pH meter immersed in the test solution measure [H₃O⁺]. (In this instrument, the two electrodes are housed in one probe.)

В

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A base is a proton acceptor, any species that accepts an H⁺ ion. A base must contain a lone pair of electrons to bind the H⁺ ion; a few examples are NH₃, CO₃²⁻, and F⁻, as well as OH⁻. Brønsted-Lowry bases are not Arrhenius bases, but all Arrhenius bases contain the Brønsted-Lowry base OH⁻.

From the Brønsted-Lowry perspective, the only requirement for an acid-base reaction is that one species donate a proton and another species accept it: an acid-base reaction is a proton-transfer process. Acid-base reactions can occur between gases, in nonaqueous solutions, and in heterogeneous mixtures, as well as in aqueous solutions.

An acid and a base always work together in the transfer of a proton. In other words, one species behaves as an acid only if another species *simultaneously* behaves as a base, and vice versa. Even when an acid or a base merely dissolves in water, an acid-base reaction occurs because water acts as the other partner. Consider two typical acidic and basic solutions:

1. Acid donates a proton to water (Figure 18.8A). When HCl dissolves in water, an H⁺ ion (a proton) is transferred from HCl to H₂O, where it becomes attached to a lone pair of electrons on the O atom, forming H₃O⁺. In effect, HCl (the acid) has donated the H⁺, and H₂O (the base) has accepted it:

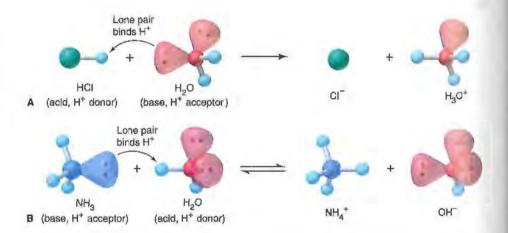
$$HCl(g) + H_2\ddot{O}(l) \longrightarrow Cl^-(aq) + H_3\ddot{O}^+(aq)$$

 Base accepts a proton from water (Figure 18.8B). In an aqueous solution of ammonia, proton transfer also occurs. An H⁺ from H₂O attaches to the N atom's lone pair, forming NH₄⁺. Having transferred an H⁺, the H₂O becomes an OH⁻ ion:

$$\ddot{N}H_3(aq) + H_2O(l) \Longrightarrow NH_4^+(aq) + OH^-(aq)$$

In this case, H₂O (the acid) has *donated* the H⁺, and NH₃ (the base) has *accepted* it. Thus, H₂O is *amphoteric*: it acts as a base in one case and as an acid in the other. As you'll see, many other species are amphoteric as well.

Figure 18.8 Proton transfer as the essential feature of a Brønsted-Lowry acid-base reaction. A, When HCl dissolves in water, it acts as an acid by donating a proton to water, which acts as a base by accepting it. B, in aqueous solution, NH₃ acts as a base by accepting a proton from water, which acts as an acid by donating it. Thus, in the Brønsted-Lowry sense, an acid-base reaction occurs in both cases.



The Conjugate Acid-Base Pair

The Brønsted-Lowry definition provides a new way to look at acid-base reactions because it focuses on the reactants *and* the products. For example, let's examine the reaction between hydrogen sulfide and ammonia:

$$H_2S + NH_3 \Longrightarrow HS^- + NH_4^+$$

In the forward reaction, H_2S acts as an acid by donating an H^+ to NH_3 , which acts as a base. The reverse reaction involves another acid-base pair. The ammonium ion, NH_4^+ , acts as an acid by donating an H^+ to the hydrogen sulfide ion,

 ${\rm HS}^-$, which acts as a base. Notice that the acid, ${\rm H_2S}$, becomes a base, ${\rm HS}^-$, and the base, ${\rm NH_3}$, becomes an acid, ${\rm NH_4}^+$.

In Brønsted-Lowry terminology, H₂S and HS⁻ are a conjugate acid-base pair: HS⁻ is the conjugate base of the acid H₂S. Similarly, NH₃ and NH₄⁺ form a conjugate acid-base pair: NH₄⁺ is the conjugate acid of the base NH₃. Every acid has a conjugate base, and every base has a conjugate acid. Thus, for any conjugate acid-base pair,

- . The conjugate base has one fewer H and one more minus charge than the acid.
- . The conjugate acid has one more H and one fewer minus charge than the base.

A Brønsted-Lowry acid-base reaction occurs when an acid and a base react to form their conjugate base and conjugate acid, respectively:

Table 18.4 shows some Brønsted-Lowry acid-base reactions. Notice that

- Each reaction has an acid and a base as reactants and as products, and these comprise two conjugate acid-base pairs.
- · Acids and bases can be neutral, cationic, or anionic.
- The same species can be an acid or a base, depending on the other species reacting. Water behaves this way in reactions 1 and 4, and HPO₄²⁻ does so in reactions 4 and 6.

Table 18.4 The Conjugate Pairs in Some Acid-Base Reactions

| | | | Conjugate Pair | | | | |
|------------|--------------------------------|---|------------------|---|--------------------------------|---|-------------------------------|
| | Acid | + | Base | | Base | + | Acid |
| | | | | C | onjugate Pair | | |
| Reaction 1 | HF | + | H ₂ O | | F ⁻ | + | H ₃ O ⁺ |
| Reaction 2 | HCOOH | + | CN- | = | HCOO- | + | HCN |
| Reaction 3 | NH ₄ ⁺ | + | CO_3^{2-} | = | NH ₃ | + | HCO ₃ |
| Reaction 4 | H ₂ PO ₄ | + | OH- | = | HPO ₄ ²⁻ | + | H ₂ O |
| Reaction 5 | H ₂ SO ₄ | + | N2H5+ | _ | HSO ₄ | + | $N_2H_6^{2+}$ |
| Reaction 6 | HPO ₄ 2- | + | SO32- | _ | PO ₄ 3- | + | HSO ₃ |

SAMPLE PROBLEM 18.4 Identifying Conjugate Acid-Base Pairs

Problem The following reactions are important environmental processes. Identify the conjugate acid-base pairs.

(a) $H_2PO_4^-(aq) + CO_3^{2-}(aq) \implies HCO_3^-(aq) + HPO_4^{2-}(aq)$

(b) $H_2O(l) + SO_3^{2-}(aq) \implies OH^{-}(aq) + HSO_3^{-}(aq)$

Plan To find the conjugate pairs, we find the species that donated an H⁺ (acid) and the species that accepted it (base). The acid (or base) on the left becomes its conjugate base (or conjugate acid) on the right. Remember, the conjugate acid has one more H and one fewer minus charge than its conjugate base.

Solution (a) $H_2PO_4^-$ has one more H^+ than $HPO_4^{\ 2^-}$; $CO_3^{\ 2^-}$ has one fewer H^+ than HCO_3^- . Therefore, $H_2PO_4^-$ and HCO_3^- are the acids, and $HPO_4^{\ 2^-}$ and $CO_3^{\ 2^-}$ are the bases. The conjugate acid-base pairs are $H_2PO_4^-/HPO_4^{\ 2^-}$ and $HCO_3^-/CO_3^{\ 2^-}$.

(b) H_2O has one more H^+ than OH^- ; SO_3^{2-} has one fewer H^+ than HSO_3^- . The acids are H_2O and HSO_3^- ; the bases are OH^- and SO_3^{2-} . The conjugate acid-base pairs are H_2O/OH^- and HSO_3^-/SO_3^{2-} .

FOLLOW-UP PROBLEM 18.4 Identify the conjugate acid-base pairs:

(a) $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

(b) $H_2O(l) + F^-(aq) \Longrightarrow OH^-(aq) + HF(aq)$

Chapter 18 Acid-Base Equilibria

Relative Acid-Base Strength and the Net Direction of Reaction

The net direction of an acid-base reaction depends on the relative strengths of the acids and bases involved. A reaction proceeds to the greater extent in the direction in which a stronger acid and stronger base form a weaker acid and weaker base. If the stronger acid and base are written on the left, the net direction is to the right, so $K_c > 1$.

The net direction of the reaction of H_2S and NH_3 is to the right ($K_c > 1$) because H_2S is a stronger acid than NH_4^+ , the other acid present, and NH_3 is a stronger base than HS^- , the other base:

H₂S + NH₃
$$\Longrightarrow$$
 HS + NH₄*

stronger acid + stronger base \longrightarrow weaker base + weaker acid

You might think of the process as a competition for the proton between the two bases, NH₃ and HS⁻, in which NH₃ wins.

Similarly, the extent of acid (HA) dissociation in water depends on a competition for the proton between the two bases, A^- and H_2O . When the acid HNO₃ dissolves in water, it transfers an H^+ to the base, H_2O , forming the conjugate base of HNO₃, which is NO₃⁻, and the conjugate acid of H_2O , which is H_3O^+ :

(In this case, the net direction is so far to the right that it would be inappropriate to show an equilibrium arrow.) HNO_3 is a stronger acid than H_3O^+ , and H_2O is a stronger base than NO_3^- . Thus, with strong acids such as HNO_3 , the H_2O wins the competition for the proton because A^- (NO_3^-) is a much weaker base. On the other hand, with weak acids such as HF, the A^- (F^-) wins because it is a stronger base than H_2O :

Based on evidence gathered from the results of many such reactions, we can rank conjugate pairs in terms of the ability of the acid to transfer its proton (Figure 18.9). Note, especially, that a weaker acid has a stronger conjugate base. This makes perfect sense: the acid gives up its proton less readily because its conjugate base holds it more strongly. We can use this list to predict the direction of a reaction between any two pairs, that is, whether the equilibrium position lies predominantly to the right $(K_c > 1)$ or to the left $(K_c < 1)$. An acid-base reaction proceeds to the right if the acid reacts with a base that is lower on the list because this combination produces a weaker conjugate base and a weaker conjugate acid.

SAMPLE PROBLEM 18.5 Predicting the Net Direction of an Acid-Base Reaction

Problem Predict the net direction and whether K_c is greater or less than 1 for each of the following reactions (assume equal initial concentrations of all species);

(a) $H_2PO_4^-(aq) + NH_3(aq) \implies NH_4^+(aq) + HPO_4^{2-}(aq)$

(b) $H_2O(l) + HS^-(aq) \Longrightarrow OH^-(aq) + H_2S(aq)$

Plan We first identify the conjugate acid-base pairs. To predict the direction, we consult Figure 18.9 to see which acid and base are stronger. The stronger acid and base form the weaker acid and base, so the reaction proceeds in that net direction. If the reaction as written proceeds to the right, then [products] is higher than [reactants], and $K_c > 1$.

Solution (a) The conjugate pairs are H₂PO₄⁻/HPO₄²⁻ and NH₄⁺/NH₃. H₂PO₄⁻ is higher on the list of acids, so it is stronger than NH₄⁺; and NH₃ is lower on the list of bases, so

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it is stronger than HPO42-. Therefore,

$$H_2PO_4^-(aq) + NH_3(aq) \implies NH_4^+(aq) + HPO_4^{2-}(aq)$$

stronger acid + stronger base \longrightarrow weaker acid + weaker base

The net direction is right, so $K_c > 1$.

(b) The conjugate pairs are H₂O/OH⁻ and H₂S/HS⁻. H₂S is higher on the list of acids, and OH⁻ is lower on the list of bases. Thus, we have

$$H_2O(l) + HS^-(aq) \Longrightarrow OH^-(aq) + H_2S(aq)$$

weaker acid + weaker base \longleftrightarrow stronger base + stronger acid

The net direction is left, so $K_c < 1$.

FOLLOW-UP PROBLEM 18.5 Explain with balanced equations, in which you show the net direction of the reaction, each of the following observations:

- (a) You smell ammonia when NH3 dissolves in water.
- (b) The odor goes away when you add an excess of HCl to the solution in part (a).
- (c) The odor returns when you add an excess of NaOH to the solution in part (b).

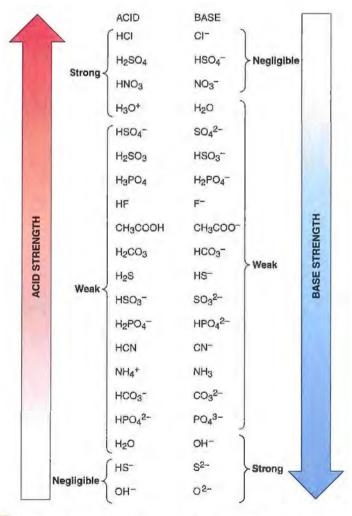


Figure 18.9 Strengths of conjugate acid-base pairs. The stronger the acid is, the weaker its conjugate base. The strongest acid appears at top left and the strongest base at bottom right. When an acid reacts with a base farther down the list, the reaction proceeds to the right ($K_c > 1$).

Chapter 18 Acid-Base Equilibria

SECTION SUMMARY

The Brønsted-Lowry acid-base definition does not require that bases contain OH or that acid-base reactions occur in aqueous solution. It defines an acid as a species that donates a proton and a base as one that accepts it. An acid and a base act together in proton transfer. When an acid donates a proton, it becomes the conjugate base; when a base accepts a proton, it becomes the conjugate acid. In an acid-base reaction, acids and bases form their conjugates. A stronger acid has a weaker conjugate base, and vice versa. Thus, the reaction proceeds in the net direction in which a stronger acid and base form a weaker base and acid.

18.4 SOLVING PROBLEMS INVOLVING WEAK-ACID EQUILIBRIA

Just as you saw in Chapter 17 for equilibrium problems in general, there are two general types of equilibrium problems involving weak acids and their conjugate bases:

- 1. Given equilibrium concentrations, find Ka.
- 2. Given K_a and some concentration information, find the other equilibrium concentrations.

For all of these problems, we'll apply the same problem-solving approach, notation system, and assumptions:

- The problem-solving approach. As always, start with what is given in the problem statement and move logically toward what you want to find. Make a habit of applying the following steps:
 - Write the balanced equation and K_a expression; these will tell you what to find.
 - 2. Define x as the unknown change in concentration that occurs during the reaction. Frequently, $x = [HA]_{dissoc}$, the concentration of HA that dissociates, which, through the use of certain assumptions, also equals $[H_3O^+]$ and $[A^-]$ at equilibrium.
 - 3. Construct a reaction table that incorporates the unknown.
 - 4. Make assumptions that simplify the calculations, usually that x is very small relative to the initial concentration.
 - 5. Substitute the values into the K_a expression, and solve for x.
 - Check that the assumptions are justified. (Apply the 5% test that was first used in Sample Problem 17.9, p. 742.) If they are not justified, use the quadratic formula to find x.
- The notation system. As always, the molar concentration of each species is shown with brackets. A subscript refers to where the species comes from or when it occurs in the reaction process. For example, [H₃O⁺]_{from HA} is the molar concentration of H₃O⁺ that comes from the dissociation of HA; [HA]_{init} is the initial molar concentration of HA, that is, before the dissociation occurs; [HA]_{dissoc} is the molar concentration of HA that dissociates; and so forth. Recall that brackets with no subscript refer to the molar concentration of the species at equilibrium.
- · The assumptions. We make two assumptions to simplify the arithmetic:
 - 1. The [H₃O⁺] from the autoionization of water is negligible. In fact, it is so much smaller than the [H₃O⁺] from the dissociation of HA that we can neglect it:

$$[H_3O^+] = [H_3O^+]_{from HA} + [H_3O^+]_{from H_2O} \approx [H_3O^+]_{from HA}$$

Indeed, Le Châtelier's principle tells us that [H₃O⁺]_{from HA} decreases the extent of autoionization of water, so [H₃O⁺]_{from H₂O} in the HA solution is even less than [H₃O⁺] in pure water. Note that each molecule of HA that

dissociates forms one H_3O^+ and one A^- , so $[A^-] = [H_3O^+]$. 2. A weak acid has a small K_a . Therefore, it dissociates to such a small extent that we can neglect the change in its concentration to find its equilibrium concentration:

$$[HA] = [HA]_{init} - [HA]_{dissoc} \approx [HA]_{init}$$

Finding Ka Given Concentrations

This type of problem involves finding K_a of a weak acid from the concentration of one of the species in solution, usually H₃O⁺ from a given pH:

$$HA(aq) + H_2O(l) \Longrightarrow H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

A common approach is to prepare an aqueous solution of HA and measure its pH. You prepared the solution, so you know [HA]_{init}. You can calculate [H₃O⁺] from the measured pH and then determine [AT] and [HA] at equilibrium from the assumptions you make. At this point, you substitute these values into the Ka expression and solve for Ka. We'll go through the entire approach in Sample Problem 18.6 and then simplify later problems by omitting some of the recurring steps.

SAMPLE PROBLEM 18.6 Finding Ka of a Weak Acid from pH of Its Solution

Problem Phenylacetic acid (C6H3CH2COOH, simplified here to HPAc; see photo) builds up in the blood of persons with phenylketonuria, an inherited disorder that, if untreated, causes mental retardation and death. A study of the acid shows that the pH of 0.12 M HPAc is 2.62. What is the K_a of phenylacetic acid?

Plan We are given [HPAc]_{init} (0.12 M) and the pH (2.62) and must find K_a . We first write the equation for HPAc dissociation and the expression for K, to see which values we need

$$HPAc(aq) + H2O(l) \rightleftharpoons H3O+(aq) + PAc-(aq) Ka = \frac{[H3O+][PAc-]}{[HPAc]}$$

• To find [H₃O⁺]: We know the pH, so we can find [H₃O⁺]. Because a pH of 2.62 is more than four pH units (104-fold) lower than the pH of pure water itself (pH = 7.0), we can assume that $[H_3O^+]_{from \ HPAc} >> [H_3O^+]_{from \ H_2O}$. Therefore, $[H_3O^+]_{from \ HPAc} + [H_3O^+]_{from \ H_2O} \approx [H_3O^+]_{from \ HPAc} \approx [H_3O^+]$.
• To find [PAc]: Because each HPAc that dissociates forms one H_3O^+ and one PAc,

· To find [HPAc]: We know [HPAc] init. Because HPAc is a weak acid, we assume that very little dissociates, so [HPAc]_{init} - [HPAc]_{dissoc} = [HPAc] ≈ [HPAc]_{init}.

We set up a reaction table, make the assumptions, substitute the equilibrium values, solve for Ka, and then check the assumptions.

Solution Calculating [H₃O⁺]:

$$[H_3O^+] = 10^{-pH} = 10^{-2.62} = 2.4 \times 10^{-3} M$$

Setting up the reaction table, with $x = [HPAc]_{dissoc} = [H_3O^+]_{from \, HPAc} = [PAc^-] \approx [H_3O^+]$:

| Concentration (M) | HPAc(aq) | + | H ₂ O(1) | - | H3O+(aq) | + | PAc (aq) |
|-------------------|----------|---|---------------------|---|-----------------------|----------------|----------|
| Initial | 0.12 | | _ | | 1×10 ⁻⁷ | | 0 |
| Change | x | | _ | | +x | | +x |
| Equilibrium | 0.12 - x | | _ | х | + (<1×10 ⁻ | ⁷) | x |



Phenylatanine, one of the amino acids that make up aspartame, is metabolized to phenylacetic acid (model).

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Making the assumptions:

1. The calculated $[H_3O^+]$ $(2.4\times10^{-3}\ M) >> [H_3O^+]_{from\ H_2O}\ (<1\times10^{-7}\ M)$, so we assume that $[H_3O^+] \approx [H_3O^+]_{from HPAc} = x$ (the change in [HPAc])

2. HPAc is a weak acid, so we assume that [HPAc] = $0.12 M - x \approx 0.12 M$. Solving for the equilibrium concentrations:

$$x \approx [\text{H}_3\text{O}^+] = [\text{PAc}^-] = 2.4 \times 10^{-3} M$$

[HPAc] = 0.12 $M - x = 0.12 M - (2.4 \times 10^{-3} M) \approx 0.12 M$ (to 2 sf)

Substituting these values into K_a :

these values into
$$K_a$$
:

$$K_a = \frac{[H_3O^+][PAc^-]}{[HPAc]} \approx \frac{(2.4 \times 10^{-3})(2.4 \times 10^{-3})}{0.12} = 4.8 \times 10^{-5}$$

Checking the assumptions by finding the percent error in concentration:

1. For $[H_3O^+]_{\text{from }H_2O}$: $\frac{1\times 10^{-7} M}{2.4\times 10^{-3} M} \times 100 = 4\times 10^{-3}\%$ (<5%; assumption is justified).

2. For [HPAc]_{dissoc}: $\frac{2.4 \times 10^{-3} M}{0.12 M} \times 100 = 2.0\%$ (<5%; assumption is justified). We had already shown above that, to two significant figures, the concentration had not changed. so this check was not really necessary.

Check The [H₃O⁺] makes sense: pH 2.62 should give [H₃O⁺] between 10⁻² and 10⁻³ M. The K_a calculation also seems in the correct range: $(10^{-3})^2/10^{-1} = 10^{-5}$, and this value seems reasonable for a weak acid.

Comment [H₃O⁺]_{from H₂O} is so small relative to [H₃O⁺]_{from HA} that, from here on, we will disregard it and enter it as zero in reaction tables.

FOLLOW-UP PROBLEM 18.6 The conjugate acid of ammonia is NH4+, a weak acid. If a 0.2 M NH₄Cl solution has a pH of 5.0, what is the K₂ of NH₄⁺?

Finding Concentrations Given Ka

The second type of equilibrium problem involving weak acids gives some concentration data and the Ka value and asks for the equilibrium concentration of some component. Such problems are very similar to those we solved in Chapter 17 in which a substance with a given initial concentration reacted to an unknown extent (see Sample Problems 17.8 to 17.10).

SAMPLE PROBLEM 18.7 Determining Concentrations from Ka and Initial [HA]

Problem Propanoic acid (CH3CH2COOH, which we simplify as HPr) is a carboxylic acid whose salts are used to retard mold growth in foods. What is the [H₃O⁺] of 0.10 M HPr $(K_n = 1.3 \times 10^{-5})$?

Plan We know the initial concentration (0.10 M) and K_a (1.3×10⁻⁵) of HPr, and we need to find $[H_3O^+]$. First, we write the balanced equation and the expression for K_a :

$$HPr(aq) + H_2O(l) \implies H_3O^+(aq) + Pr^-(aq)$$
 $K_a = \frac{[H_3O^+][Pr^-]}{[HPr]} = 1.3 \times 10^{-5}$

We know [HPr]_{init} but not [HPr]. If we let $x = [HPr]_{dissoc}$, x is also $[H_3O^+]_{from\ HPr}$ and $[Pr^-]$ because each HPr that dissociates yields one H_3O^+ and one Pr^- . With this information, we can set up a reaction table. In solving for x, we assume that, because HPr has a small K_a , it dissociates very little; therefore, $[HPr]_{init} - x = [HPr] \approx [HPr]_{init}$. After we find x, we check the assumption.

Solution Setting up a reaction table, with $x = [HPr]_{dissoc} = [H_3O^+]_{from HPr} = [Pr^-] = [H_3O^+]$;

| Concentration (M) | HPr(aq) | + | H ₂ O(l) | === | H ₃ O ⁺ (aq) | + | Pr (aq) |
|-------------------|----------|---|---------------------|-----|------------------------------------|---|---------|
| Initial | 0.10 | | _ | | 0 | | 0 |
| Change | -x | | _ | | +x | | +x |
| Equilibrium | 0.10 - x | | _ | | x | | λ, |

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Making the assumption: K_a is small, so x is small compared with [HPr]_{init}; therefore, 0.10 $M-x \approx 0.10 M$. Substituting into the K_a expression and solving for x:

$$K_{\rm a} = \frac{[{\rm H_3O}^+][{\rm Pr}^-]}{[{\rm HPr}]} = 1.3 \times 10^{-5} \approx \frac{(x)(x)}{0.10}$$

 $x \approx \sqrt{(0.10)(1.3 \times 10^{-5})} = 1.1 \times 10^{-3} M = [{\rm H_3O}^+]$

Checking the assumption:

For [HPr]_{dissoc}; $\frac{1.1 \times 10^{-3} M}{0.10 M} \times 100 = 1.1\%$ (<5%; assumption is justified).

Check The $[H_3O^+]$ seems reasonable for a dilute solution of a weak acid with a moderate K_a . By reversing the calculation, we can check the math: $(1.1\times10^{-3})^2/0.10 = 1.2\times10^{-5}$, which is within rounding of the given K_a .

Comment In these problems, we assume that the concentration of HA that dissociates $([HA]_{dissoc} = x)$ can be neglected because K_a is relatively small. However, this is true only if $[HA]_{init}$ is relatively large. Here's a benchmark to see if the assumption is justified:

- If $\frac{[HA]_{init}}{K_a} > 400$, the assumption is justified: neglecting x introduces an error < 5%.
- If $\frac{[HA]_{init}}{K_a}$ < 400, the assumption is *not* justified; neglecting x introduces an error > 5%,

so we solve a quadratic equation to find x.

The latter situation occurs in the follow-up problem.

FOLLOW-UP PROBLEM 18.7 Cyanic acid (HOCN) is an extremely acrid, unstable substance. What is the $[H_3O^+]$ and pH of 0.10 M HOCN $(K_a = 3.5 \times 10^{-4})$?

The Effect of Concentration on the Extent of Acid Dissociation

If we repeat the calculation in Sample Problem 18.7, but start with a lower [HPr], we observe a very interesting fact about the extent of dissociation of a weak acid. Suppose the initial concentration of HPr is one-tenth as much, $0.010\,M$ rather than $0.10\,M$. After filling in the reaction table and making the same assumptions, we find that

$$x = [HPr]_{dissoc} = 3.6 \times 10^{-4} M$$

Now, let's compare the percentages of HPr molecules dissociated at the two different initial acid concentrations, using the relationship

Percent HA dissociated =
$$\frac{[HA]_{dissoc}}{[HA]_{init}} \times 100$$
 (18.5)

Case 1: $[HPr]_{init} = 0.10 M$

Percent dissociated =
$$\frac{1.1 \times 10^{-3} M}{1.0 \times 10^{-1} M} \times 100 = 1.1\%$$

Case 2: $[HPr]_{init} = 0.010 M$

Percent dissociated =
$$\frac{3.6 \times 10^{-4} M}{1.0 \times 10^{-2} M} \times 100 = 3.6\%$$

As the initial acid concentration decreases, the percent dissociation of the acid increases. Don't confuse the concentration of HA dissociated with the percent HA dissociated. The [HA]_{dissoc} is lower in the diluted HA solution because the actual number of dissociated HA molecules is smaller. It is the fraction (and thus the percent) of dissociated HA molecules that increases with dilution.

This phenomenon is analogous to a change in container volume (pressure) for gases at equilibrium (see the discussion in Section 17.6). In that situation, an increase in volume shifts the equilibrium position to favor more moles of gas. In the case of HA dissociation, the available volume increases as solvent is added and the solution is diluted; this increase in volume shifts the equilibrium position to favor more moles of ions.

Chapter 18 Acid-Base Equilibria

The Behavior of Polyprotic Acids

Acids with more than one ionizable proton are **polyprotic acids**. In a solution of a polyprotic acid, one proton at a time dissociates from the acid molecule, and each dissociation step has a different K_a . For example, phosphoric acid is a triprotic acid (three ionizable protons), so it has three K_a values:

$$H_{3}PO_{4}(aq) + H_{2}O(l) \Longrightarrow H_{2}PO_{4}^{-}(aq) + H_{3}O^{+}(aq)$$

$$K_{a1} = \frac{[H_{2}PO_{4}^{-}][H_{3}O^{+}]}{[H_{3}PO_{4}]} = 7.2 \times 10^{-3}$$

$$H_{2}PO_{4}^{-}(aq) + H_{2}O(l) \Longrightarrow HPO_{4}^{2-}(aq) + H_{3}O^{+}(aq)$$

$$K_{a2} = \frac{[HPO_{4}^{2-}][H_{3}O^{+}]}{[H_{2}PO_{4}^{-}]} = 6.3 \times 10^{-8}$$

$$HPO_{4}^{2-}(aq) + H_{2}O(l) \Longrightarrow PO_{4}^{3-}(aq) + H_{3}O^{+}(aq)$$

$$K_{a3} = \frac{[PO_{4}^{3-}][H_{3}O^{+}]}{[HPO_{4}^{2-}]} = 4.2 \times 10^{-13}$$

As you can see from the relative K_a values, H_3PO_4 is a much stronger acid than $H_2PO_4^-$, which is much stronger than HPO_4^{2-} . Table 18.5 lists some common polyprotic acids and their K_a values. (A more extensive list is presented in Appendix C.) Notice that, in every case, the first proton comes off to a much greater extent than the second and, where applicable, the second ionizes to a much greater extent than the third:

$$K_{\rm al} > K_{\rm a2} > K_{\rm a3}$$

This trend makes sense: it is more difficult for an H^+ ion to leave a singly charged anion (such as $H_2PO_4^-$) than to leave a neutral molecule (such as H_3PO_4), and more difficult still for it to leave a doubly charged anion $(HPO_4^{\ 2^-})$. Successive acid dissociation constants typically differ by several orders of magnitude. This fact greatly simplifies pH calculations involving polyprotic acids because we can usually neglect the H_3O^+ coming from the subsequent dissociations.

| Name (Formula) | alues for Some Polyprotic A Lewis Structure* | Kat | K _{a2} | K _{a3} | |
|---|---|----------------------|-----------------------|-----------------------|-------------|
| Oxalic acid (H ₂ C ₂ O ₄) | :0: :0: H—Ö—C—C—Ö—H | 5.6×10 ⁻² | 5.4×10 ⁻⁵ | | 4 |
| Sulfurous acid (H ₂ SO ₃) | :0: Н—ё—ё—ё—н | 1.4×10^{-2} | 6.5×10 ⁻⁸ | | |
| Phosphoric acid (H ₃ PO ₄) | :0: Н—Ö—Р—Ö—Н :О—Н | 7.2×10 ⁻³ | 6.3×10 ⁻⁸ | 4.2×10 ⁻¹³ | |
| Arsenic acid (H ₃ AsO ₄) | H−Ö−As−Ö−H :Ö−H | 6×10 ⁻³ | 1.1×10 ⁻⁷ | 3×10 ⁻¹² | A Pin Paris |
| Carbonic acid (H ₂ CO ₃) | н—ё—с—ё—н :0: | 4.5×10 ⁻⁷ | 4.7×10 ⁻¹¹ | | |
| Hydrosulfuric acid (H ₂ S) | н— Ё—н | 9×10 ⁻⁸ | 1×10 ⁻¹⁷ | | |

^{*}Red type indicates the ionizable protons.

SAMPLE PROBLEM 18.8 Calculating Equilibrium Concentrations for a Polyprotic Acid

Problem Ascorbic acid ($H_2C_6H_6O_6$; H_2 Asc for this problem), known as vitamin C, is a diprotic acid ($K_{a1} = 1.0 \times 10^{-5}$ and $K_{a2} = 5 \times 10^{-12}$) found in citrus fruit. Calculate [H₂Asc], [HAsc], [Asc²], and the pH of 0.050 M H₂Asc.

Plan We know the initial concentration (0.050 M) and both K_a 's for H_2Asc , and we have to calculate the equilibrium concentrations of all species and convert [H₃O⁺] to pH. We first write the equations and K_a expressions:

$$H_2Asc(aq) + H_2O(l) \implies HAsc^-(aq) + H_3O^+(aq)$$
 $K_{a1} = \frac{[HAsc^-][H_3O^+]}{[H_2Asc]} = 1.0 \times 10^{-5}$
 $HAsc^-(aq) + H_2O(l) \implies Asc^{2-}(aq) + H_3O^+(aq)$ $K_{a2} = \frac{[Asc^{2-}][H_3O^+]}{[HAsc^-]} = 5 \times 10^{-12}$

$$HAsc^{-}(aq) + H_2O(l) \implies Asc^{2-}(aq) + H_3O^{+}(aq)$$
 $K_{a2} = \frac{[Asc^{2-}][H_3O^{+}]}{[HAsc^{-}]} = 5 \times 10^{-12}$

Then we assume the following:

1. Because $K_{a1} >> K_{a2}$, dissociation of the first proton produces almost all the H_3O^+ : $[H_3O^+]_{from\ H_2Asc} >> [H_3O^+]_{from\ HAsc}$

2. Because Ka1 is small, the amount of H2Asc that dissociates can be neglected relative to the initial concentration: [H2Asc]init = [H2Asc].

We set up a reaction table for the first dissociation, with x equal to the concentration of H₂Asc that dissociates, and then solve for [H₃O⁺] and [HAsc⁻]. Because the second dissociation occurs to a much lesser extent than the first, we can substitute values from the first directly to find [Asc2-] of the second.

Solution Setting up a reaction table with $x = [H_2Asc]_{dissoc} = [HAsc] \approx [H_3O^+]$:

| Concentration (M) | H ₂ Asc(aq) | + | $H_2O(l)$ | = | H ₃ O ⁺ (aq) | + | HAsc (aq) |
|-------------------|------------------------|---|-----------|---|------------------------------------|---|-----------|
| Initial | 0.050 | | _ | | 0 | | 0 |
| Change | -x | | | | +x | | +x |
| Equilibrium | 0.050 - x | | _ | | x | | X |

Making the assumptions:

1. Because $K_{a2} \ll K_{a1}$, $[H_3O^+]_{from HAsc^-} \ll [H_3O^+]_{from H_2Asc}$. Therefore,

$$[H_3O^+]_{from\ H_2Asc} \approx [H_3O^+]$$

2. Because K_{a1} is small, $[H_2Asc]_{init} - x = [H_2Asc] \approx [H_2Asc]_{init}$. Thus,

$$[H_2Asc] = 0.050 M - x \approx 0.050 M$$

Substituting into the expression for K_{al} and solving for x:

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HAsc}^-]}{[\text{H}_2\text{Asc}]} = 1.0 \times 10^{-5} \approx \frac{x^2}{0.050}$$

 $x = [\text{HAsc}^-] \approx [\text{H}_3\text{O}^+] \approx 7.1 \times 10^{-4} M$
 $pH = -\log [\text{H}_3\text{O}^+] = -\log (7.1 \times 10^{-4}) = 3.15$

Checking the assumptions:

1. $[H_3O^+]_{from \; HAsc^-} << [H_3O^+]_{from \; H_2Asc}$: For any second dissociation that does occur, we have

$$[H_3O^+]_{from \, HAsc^-} \approx \sqrt{[HAsc^-](K_{a2})} = \sqrt{(7.1 \times 10^{-4})(5 \times 10^{-12})} = 6 \times 10^{-8} \, M$$

This is even less than [H₃O⁺]_{from H₂O}, so the assumption is justified.

2.
$$[H_2Asc]_{dissoc} << [H_2Asc]_{init}$$
: $\frac{7.1 \times 10^{-4} M}{0.050 M} \times 100 = 1.4\%$ (<5%; assumption is justified).

Also, from the Comment in Sample Problem 18.7, note that

$$\frac{[\text{H}_2\text{Asc}]_{\text{init}}}{K_{\text{n1}}} = \frac{0.050}{1.0 \times 10^{-5}} = 5000 > 400$$

Calculating [Asc²⁻]:

$$K_{a2} = \frac{[H_3O^+][Asc^2]}{[HAsc^-]}$$
 and $[Asc^2] = \frac{(K_{a2})[HAsc^2]}{[H_3O^+]}$
 $[Asc^2] = \frac{(5 \times 10^{-12})(7.1 \times 10^{-4})}{7.1 \times 10^{-4}} = 5 \times 10^{-12} M$

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Check $K_{a1} >> K_{a2}$, so it makes sense that [HAsc⁻] >> [Asc²⁻] because Asc²⁻ is produced only in the second (much weaker) dissociation. Both K_a 's are small, so all concentrations except [H₂Asc] should be much lower than the original 0.050 M.

FOLLOW-UP PROBLEM 18.8 Oxalic acid (HOOC—COOH, or $H_2C_2O_4$) is the simplest diprotic carboxylic acid. Its commercial uses include bleaching straw and leather and removing rust and ink stains. Calculate $[H_2C_2O_4]$, $[HC_2O_4^{-}]$, $[C_2O_4^{-2}]$, and the pH of a 0.150 M $H_2C_2O_4$ solution. Use K_a values from Appendix C.

SECTION SUMMARY

Two common types of weak-acid equilibrium problems involve finding K_a from a concentration and finding a concentration from K_a . We summarize the information in a reaction table, and we simplify the arithmetic by assuming (1) $[H_3O^+]_{from\ H_2O}$ is so small relative to $[H_3O^+]_{from\ HA}$ that it can be neglected, and (2) weak acids dissociate so little that $[HA]_{init} \approx [HA]$ at equilibrium. The fraction of weak acid molecules that dissociates is greater in a more dilute solution, even though the total $[H_3O^+]$ is less. Polyprotic acids have more than one ionizable proton, but we assume that the first dissociation provides virtually all the H_3O^+ .

18.5 WEAK BASES AND THEIR RELATION TO WEAK ACIDS

By focusing on where the proton comes from and goes to, the Brønsted-Lowry concept expands the definition of a base to encompass a host of species that the Arrhenius definition excludes: a base is any species that accepts a proton; to do so, the base must have a lone electron pair. (The lone electron pair also plays the central role in the Lewis acid-base definition, as you'll see later in this chapter.)

Now let's examine the equilibrium system of a weak base and focus, as we did for weak acids, on aqueous solutions. When a base (B) dissolves, it accepts a proton from H₂O, which acts here as an acid, leaving behind an OH⁻ ion:

$$B(aq) + H_2O(aq) \Longrightarrow BH^+(aq) + OH^-(aq)$$

This general reaction for a base in water is described by the following equilibrium expression:

$$K_{c} = \frac{[BH^{+}][OH^{-}]}{[B][H_{2}O]}$$

Based on our earlier reasoning that $[H_2O]$ is treated as a constant in aqueous reactions, we include $[H_2O]$ in the value of K_c and obtain the base-dissociation constant (or base-ionization constant), K_b :

$$K_{\rm b} = \frac{[{\rm BH}^+][{\rm OH}^-]}{[{\rm B}]}$$
 (18.6)

Despite the name "base-dissociation constant," no base dissociates in the process, as you can see from the reaction.

As in the relation between pK_a and K_a , we know that pK_b , the negative logarithm of the base-dissociation constant, decreases with increasing K_b (that is, increasing base strength). In aqueous solution, the two large classes of weak bases are nitrogen-containing molecules, such as ammonia and the amines, and the anions of weak acids.

Molecules as Weak Bases: Ammonia and the Amines

Ammonia is the simplest nitrogen-containing compound that acts as a weak base in water:

$$NH_3(aq) + H_2O(l) \implies NH_4^+(aq) + OH^-(aq)$$
 $K_b = 1.76 \times 10^{-5} \text{ (at 25°C)}$

| Name (Formula) | Lewis Structure* | Kb | |
|---|-----------------------|-----------------------|---------------|
| Diethylamine [(CH ₃ CH ₂) ₂ NH] | H H H H H H | 8.6×10 ⁻⁴ | 1 |
| Dimethylamine [(CH ₃) ₂ NH] | H—C—Й—С—Н Н Н Н | 5.9×10 ⁻⁴ | |
| Methylamine (CH ₃ NH ₂) | H—C—N—H H—H H—H | 4.4×10 ⁻⁴ | BASE STRENGTH |
| Ammonia (NH ₃) | H—N—H | 1.76×10^{-5} | BASE |
| Pyridine (C ₅ H ₅ N) | On: | 1.7×10 ⁻⁹ | |
| Aniline (C ₆ H ₅ NH ₂) | <u>№</u> н Н | 4.0×10 ⁻¹⁰ | |

^{*}Blue type indicates the basic nitrogen and its lone pair.

Despite labels on reagent bottles that read "ammonium hydroxide," an aqueous solution of ammonia consists largely of unprotonated NH₃ molecules, as you can see from its small K_b value. In a 1.0 M NH₃ solution, for example, $[OH^-] = [NH_4^+] = 4.2 \times 10^{-3}$ M, so about 99.58% of the NH₃ is not ionized. Table 18.6 shows the K_b values for a few common molecular bases. (A more extensive list appears in Appendix C.)

If one or more of the H atoms in NH₃ is replaced by an organic group (designated as R), an *amine* results: RNH₂, R₂NH, or R₃N (Section 15.4; see Figure 15.15). The key structural feature of these organic compounds, as in all Brønsted-Lowry bases, is a lone pair of electrons that can bind the proton donated by the acid. Figure 18.10 depicts this process for methylamine, the simplest amine.

Finding the pH of a solution of a molecular weak base is a problem very similar to the type involving a weak acid. We write the equilibrium expression, set up a reaction table to find [base]_{reacting}, make the usual assumptions, and then solve for $[OH^-]$. The main difference is that we must convert $[OH^-]$ to $[H_3O^+]$ in order to calculate pH.

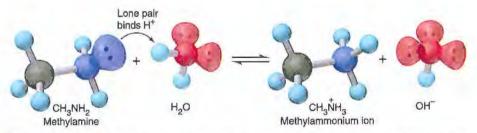


Figure 18.10 Abstraction of a proton from water by methylamine. The amines are organic derivatives of ammonia. Methylamine, the simplest amine, acts as a base in water by accepting a proton, thereby increasing [OH⁻].



Chapter 18 Acid-Base Equilibria

SAMPLE PROBLEM 18.9 Determining pH from Kb and Initial [B]

Problem Dimethylamine, $(CH_3)_2NH$ (see margin), a key intermediate in detergent manufacture, has a K_b of 5.9×10^{-4} . What is the pH of 1.5 M $(CH_3)_2NH$? **Plan** We know the initial concentration (1.5 M) and K_b (5.9×10⁻⁴) of $(CH_3)_2NH$ and have

to find the pH. The amine reacts with water to form OH⁻, so we have to find $[OH^-]$ and then calculate $[H_3O^+]$ and pH. The balanced equation and K_b expression are

$$(CH_3)_2NH(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH_2^+(aq) + OH^-(aq)$$

$$K_b = \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]}$$

Because $K_b >> K_w$, the [OH⁻] from the autoionization of water is negligible, and we disregard it. Therefore,

$$[OH^{-}]_{from base} = [(CH_3)_2NH_2^{+}] = [OH^{-}]$$

Because K_b is small, we assume that the amount of amine reacting is small, so

$$[(CH_3)_2NH]_{init} - [(CH_3)_2NH]_{reacting} = [(CH_3)_2NH] \approx [(CH_3)_2NH]_{init}$$

We proceed as usual, setting up a reaction table, making the assumption, and solving for x. Then we check the assumption and convert $[OH^-]$ to $[H_3O^+]$ using K_w ; finally, we calculate pH.

Solution Setting up the reaction table, with

$$x = [(CH_3)_2NH]_{reacting} = [(CH_3)_2NH_2^+] = [OH^-]$$

| Concentration (M) | (CH ₃) ₂ NH(aq) | + | $H_2O(l)$ | (CH ₃) ₂ NH ₂ ⁺ (aq) | + | $OH^-(aq)$ |
|-------------------|--|---|-----------|---|---|------------|
| Initial | 1.5 | | - | 0 | | 0 |
| Change | -x | | _ | +x | | +x |
| Equilibrium | 1.5 - x | | - | \boldsymbol{x} | | х |

Making the assumption:

 K_b is small, so $[(CH_3)_2NH]_{init} \approx [(CH_3)_2NH]$; thus, 1.5 $M-x \approx 1.5 M$. Substituting into the K_b expression and solving for x:

$$K_{b} = \frac{[(CH_{3})_{2}NH_{2}^{+}][OH^{-}]}{[(CH_{3})_{2}NH]}$$
$$= 5.9 \times 10^{-4} \approx \frac{x^{2}}{1.5}$$
$$x = [OH^{-}] \approx 3.0 \times 10^{-2} M$$

Checking the assumption:

$$\frac{3.0 \times 10^{-2} M}{1.5 M} \times 100 = 2.0\%$$
 (<5%; assumption is justified)

Note that the Comment in Sample Problem 18.7 applies to weak bases as well:

$$\frac{[B]_{\text{init}}}{K_b} = \frac{1.5}{5.9 \times 10^{-4}} = 2.5 \times 10^3 > 400$$

Calculating pH:

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-2}} = 3.3 \times 10^{-13} M$$

$$pH = -\log (3.3 \times 10^{-13})$$

$$= 12.48$$

Check The value of x seems reasonable: $\sqrt{(-6\times10^{-4})(1.5)} = \sqrt{9\times10^{-4}} = 3\times10^{-2}$. Because (CH₃)₂NH is a weak base, the pH should be several pH units greater than 7.

FOLLOW-UP PROBLEM 18.9 Pyridine (C_5H_5N , see margin) plays a major role in organic syntheses as a solvent and base. It has a p K_b of 8.77. What is the pH of 0.10 M pyridine?



Pyridine

Anions of Weak Acids as Weak Bases

The other large group of Brønsted-Lowry bases consists of anions of weak acids:*

$$A^{-}(aq) + H_2O(l) \Longrightarrow HA(aq) + OH^{-}(aq) \qquad K_b = \frac{[HA][OH^{-}]}{[A^{-}]}$$

For example, F-, the anion of the weak acid HF, acts as a weak base:

$$F^-(aq) + H_2O(l) \Longrightarrow HF(aq) + OH^-(aq)$$
 $K_b = \frac{[HF][OH^-]}{[F^-]}$

Why is a solution of HA acidic and a solution of A basic? Let's approach the question by examining the relative concentrations of species present in 1 M HF and in 1 M NaF:

1. The acidity of HA(aq). Because HF is a weak acid, most of the HF exists in undissociated form. A small fraction of the HF molecules do dissociate, donating their protons to H_2O and yielding small concentrations of H_3O^+ and F^- . The equilibrium position of the system lies far to the left:

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

Water molecules also contribute minute amounts of H₃O⁺ and OH⁻, but these concentrations are extremely small:

$$2H_2O(l) \implies H_3O^+(aq) + OH^-(aq)$$

Of all the species present—HF, H_2O , H_3O^+ , F^- , and OH^- —the two that can influence the acidity of the solution are H_3O^+ , predominantly from HF, and OH^- from water. The solution is acidic because $[H_3O^+]_{from\ HF} >> [OH^-]_{from\ H_2O}$.

2. The basicity of $A^-(aq)$. Now, consider the species present in 1 M.NaF. The salt dissociates completely to yield a relatively large concentration of F^- . The Na⁺ ion behaves as a spectator, but some F^- reacts as a weak base with water to produce a very small amount of HF (and of OH⁻):

$$F^-(aq) + H_2O(l) \Longrightarrow HF(aq) + OH^-(aq)$$

As before, water dissociation contributes minute amounts of H_3O^+ and OH^- . Thus, in addition to the Na^+ ion, the species present are the same as in the HF solution: HF, H_2O , H_3O^+ , F^- , and OH^- . The two species that affect the acidity are OH^- , predominantly from the F^- reaction with water, and H_3O^+ from water. In this case, $[OH^-]_{from\ F^-} >> [H_3O^+]_{from\ H_2O}$, so the solution is basic.

To summarize, the factor that determines the acidity or basicity of an HA solution or an A⁻ solution is the relative concentration of HA versus A⁻ in each solution:

- In an HA solution, [HA] >> [A⁻] and [H₃O⁺]_{from HA} >> [OH⁻]_{from H₂O}, so the solution is acidic.
- In an A⁻ solution, [A⁻] >> [HA] and [OH⁻]_{from A⁻} >> [H₃O⁺]_{from H₂O}, so the solution is basic.

The Relation Between Ka and Kb of a Conjugate Acid-Base Pair

An important relationship exists between the K_a of HA and the K_b of A⁻, which we can see by treating the two dissociation reactions as a reaction sequence and adding them together:

$$\frac{\text{HA} + \text{H}_2\text{O} \Longrightarrow \text{H}_3\text{O}^+ + \text{A}^-}{\text{A}^- + \text{H}_2\text{O} \Longrightarrow \text{HA} + \text{OH}^-}$$

$$2\text{H}_2\text{O} \Longrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$$

^{*}This equation and equilibrium expression are sometimes referred to as a *hydrolysis reaction* and a *hydrolysis constant*, $K_{\rm h}$, because water is dissociated (hydrolyzed), and its parts end up in the products. Actually, except for the charge on the base, this process is the same as the proton-abstraction process with molecular bases such as ammonia, so a new term and equilibrium constant are unnecessary. That is, $K_{\rm h}$ is just another symbol for $K_{\rm b}$, so we'll use $K_{\rm b}$ throughout.

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or

The sum of the two dissociation reactions is the autoionization of water. Recall from Chapter 17 that, for a reaction that is the sum of two or more reactions, the overall equilibrium constant is the product of the individual equilibrium constants, Therefore, writing the expressions for each reaction gives

$$\frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-]$$

$$K_a \times K_b = K_w$$
 (18.7)

This relationship allows us to find K_a of the acid in a conjugate pair given K_b of the base, and vice versa. Let's use this relationship to obtain a key piece of data for solving equilibrium problems. Reference tables typically have K_a and K_b values for molecular species only. The K_b for F^- or the K_a for $CH_3NH_3^+$, for example, does not appear in standard tables, but you can calculate either value simply by looking up the value for the molecular conjugate species and relating it to K_w . To find the K_b value for F^- , for instance, we look up the K_a value for HF and relate it to K_w :

So, we have
$$K_a$$
 of HF = 6.8×10^{-4} (from Appendix C)
 K_a of HF \times K_b of F⁻ = K_w
or K_b of F⁻ = $\frac{K_w}{K_a}$ of HF = $\frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}}$ = 1.5×10^{-11}

We can use this calculated K_b value to finish solving the problem.

SAMPLE PROBLEM 18.10 Determining the pH of a Solution of A

Problem Sodium acetate (CH₃COONa, or NaAc for this problem) has applications in photographic development and textile dyeing. What is the pH of 0.25 M NaAc? K_a of acetic acid (HAc) is 1.8×10^{-5} .

Plan From the formula (NaAc) and the fact that all sodium salts are water soluble, we know that the initial concentration of acetate ion, Ac^- , is 0.25 M. We also know the K_a of the parent acid, HAc (1.8×10⁻⁵). We have to find the pH of the solution of Ac^- , which acts as a base in water:

Ac⁻
$$(aq) + H_2O(l) \Longrightarrow HAc(aq) + OH^-(aq)$$
 $K_b = \frac{[HAc][OH^-]}{[Ac^-]}$

If we calculate $[OH^-]$, we can find $[H_3O^+]$ and convert it to pH. To solve for $[OH^-]$, we need the K_b of Ac^- , which we obtain from the K_a of HAc and K_w . All sodium salts are soluble, so we know that $[Ac^-] = 0.25 \, M$. Our usual assumption is that $[Ac^-]_{init} \approx [Ac^-]$. Solution Setting up the reaction table, with $x = [Ac^-]_{reacting} = [HAc] = [OH^-]$:

| Concentration (M) | Ac (aq) | + | $H_2O(I)$ | - | HAc(aq) | + | OH [aq] |
|---------------------|---|----------------|--|-----------------------|------------------|---|---------|
| Initial | 0.25 | | - | | 0 | | 0 |
| Change | $-\chi$ | | - | | +x | | +x |
| Equilibrium | 0.25 - x | | _ | | \boldsymbol{x} | | x |
| Solving for K_b : | $K_{\rm b} = \frac{K_{\rm w}}{K_{\rm a}}$ | $=\frac{1}{1}$ | 0×10^{-14} 8×10^{-5} | = 5.6×10 ⁻ | 10 | | |

Making the assumption: Because K_b is small, 0.25 $M-x\approx 0.25~M$. Substituting into the expression for K_b and solving for x:

$$K_{\rm b} = \frac{[{\rm HAc}][{\rm OH}^-]}{[{\rm Ac}^-]} = 5.6 \times 10^{-10} \approx \frac{x^2}{0.25}$$
 $x = [{\rm OH}^-] \approx 1.2 \times 10^{-5} M$

Checking the assumption:

$$\frac{1.2 \times 10^{-5} M}{0.25 M} \times 100 = 4.8 \times 10^{-3} \% \text{ (<5\%; assumption is justified)}$$

Note that
$$\frac{0.25}{5.6 \times 10^{-10}} = 4.5 \times 10^8 > 400$$

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Solving for pH:

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.2 \times 10^{-5}} = 8.3 \times 10^{-10} M$$

 $pH = -\log (8.3 \times 10^{-10}) = 9.08$

Check The K_b calculation seems reasonable: $\sim 10 \times 10^{-15}/2 \times 10^{-5} = 5 \times 10^{-10}$. Because Ac^- is a weak base, $[OH^-] > [H_3O^+]$; thus, pH > 7, which makes sense.

FOLLOW-UP PROBLEM 18.10 Sodium hypochlorite (NaClO) is the active ingredient in household laundry bleach. What is the pH of 0.20 M NaClO?

SECTION SUMMARY

The extent to which a weak base accepts a proton from water to form OH $^-$ is expressed by a base-dissociation constant, $K_{\rm b}$. Brønsted-Lowry bases include NH $_3$ and amines and the anions of weak acids. All produce basic solutions by accepting H $^+$ from water, which yields OH $^-$ and thus makes [H $_3$ O $^+$] < [OH $^-$]. A solution of HA is acidic because [HA] >> [A $^-$], so [H $_3$ O $^+$] > [OH $^-$]. A solution of A $^-$ is basic because [A $^-$] >> [HA], so [OH $^-$] > [H $_3$ O $^+$]. By multiplying the expressions for K_a of HA and K_b of A $^-$, we obtain K_w . This relationship allows us to calculate either K_a of BH $^+$, the cationic conjugate acid of a molecular weak base B, or K_b of A $^-$, the anionic conjugate base of a molecular weak acid HA.

18.6 MOLECULAR PROPERTIES AND ACID STRENGTH

The strength of an acid depends on its ability to donate a proton, which depends in turn on the strength of the bond to the acidic proton. In this section, we apply trends in atomic and bond properties to determine the trends in acid strength of nonmetal hydrides and oxoacids and discuss the acidity of hydrated metal ions.

Trends in Acid Strength of Nonmetal Hydrides

Two factors determine how easily a proton is released from a nonmetal hydride: the electronegativity of the central nonmetal (E) and the strength of the E—H bond. Figure 18.11 displays two periodic trends:

1. Across a period, nonmetal hydride acid strength increases. Across a period, the electronegativity of the nonmetal E determines the trend. As E becomes more electronegative, electron density around H is withdrawn, and the E—H bond becomes more polar. As a result, an H^+ is released more easily to an O atom of a surrounding water molecule. In aqueous solution, the hydrides of Groups 3A(13) to 5A(15) do not behave as acids, but an increase in acid strength is seen in Groups 6A(16) and 7A(17). Thus, HCl is a stronger acid than H_2S because Cl is more electronegative (EN = 3.0) than S (EN = 2.5). The same relationship holds across each period.

2. Down a group, nonmetal hydride acid strength increases. Down a group, E—H bond strength determines the trend. As E becomes larger, the E—H bond becomes longer and weaker, so H⁺ comes off more easily.* Thus, the hydrohalic acids increase in strength down the group:

A similar trend in increasing acid strength is seen down Group 6A(16). (The trend in hydrohalic acid strength is not seen in aqueous solution, where HCl, HBr, and HI are all equally strong; we discuss how this trend is observed in Section 18.8.)

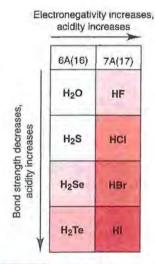


Figure 18.11 The effect of atomic and molecular properties on nonmetal hydride acidity. As the electronegativity of the nonmetal (E) bonded to the ionizable proton increases (left to right), the acidity increases. As the length of the E—H bond increases (top to bottom), the bond strength decreases, so the acidity increases. (In water, HCI, HBr, and HI are equally strong, for reasons discussed in Section 18.8.)

^{*}Actually, bond energy refers to bond breakage that forms an H atom, whereas acidity refers to bond breakage that forms an H * ion, so the two processes are not the same. Nevertheless, the magnitudes of the two types of bond breakage parallel each other.

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Trends in Acid Strength of Oxoacids

All oxoacids have the acidic H atom bonded to an O atom, so bond strength (length) is not a factor in their acidity, though it is with the nonmetal hydrides. Rather, as you saw in Section 14.8, two factors determine the acid strength of oxoacids: the electronegativity of the central nonmetal (E) and the number of O atoms.

1. For oxoacids with the same number of oxygens around E, acid strength increases with the electronegativity of E. Consider the hypohalous acids (written here as HOE, where E is a halogen atom). The more electronegative E is, the more electron density it pulls from the O—H bond; the more polar the O—H bond becomes, the more easily H^+ is lost (Figure 18.12A). Because electronegativity decreases down the group, we predict that acid strength decreases: HOCl > HOBr > HOI. Our prediction is confirmed by the K_a values:

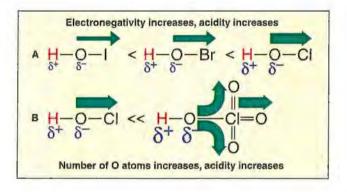
 K_a of HOCl = 2.9×10^{-8} K_a of HOBr = 2.3×10^{-9} K_a of HOI = 2.3×10^{-11} We also predict (correctly) that in Group 6A(16), H_2SO_4 is stronger than H_2SeO_4 ; in Group 5A(15), H_3PO_4 is stronger than H_3AsO_4 , and so forth.

2. For oxoacids with different numbers of oxygens around a given E, acid strength increases with number of O atoms. The electronegative O atoms pull electron density away from E, which makes the O—H bond more polar. The more O atoms present, the greater the shift in electron density, and the more easily the H^+ ion comes off (Figure 18.12B). Therefore, we predict, for instance, that chlorine oxoacids (written here as HOClO_n , with n from 0 to 3) increase in strength in the order $\mathrm{HOCl} < \mathrm{HOClO} < \mathrm{HOClO}_2 < \mathrm{HOClO}_3$. Once again, the K_a values support the prediction:

 K_a of HOCl (hypochlorous acid) = 2.9×10^{-8} K_a of HClO₂ (chlorous acid) = 1.12×10^{-2} K_a of HOClO₂ (chloric acid) ≈ 1 K_a of HOClO₃ (perchloric acid) = $>10^7$

It follows from this that HNO₃ is stronger than HNO₂, that H₂SO₄ is stronger than H₂SO₃, and so forth.

Figure 18.12 The relative strengths of oxoacids. A, Among these hypohalous acids, HOCI is the strongest and HOI the weakest. Because CI is the most electronegative of the halogens shown here, it withdraws electron density (indicated by thickness of green arrow) from the O—H bond most effectively, making that bond most polar in HOCI (indicated by the relative sizes of the § symbols). B, Among the chlorine oxoacids, the additional O atoms in HOCIO₃ pull electron density from the O—H bond, making the bond much more polar than that in HOCI.



Acidity of Hydrated Metal Ions

The aqueous solutions of certain metal ions are acidic because the *hydrated* metal ion transfers an H⁺ ion to water. Consider a general metal nitrate, M(NO₃)_n, as it dissolves in water. The ions separate and become bonded to a specific number

of surrounding H_2O molecules. This equation shows the hydration of the cation (M^{n+}) with H_2O molecules; hydration of the anion (NO_3^-) is indicated by (aq):

$$M(NO_3)_n(s) + xH_2O(l) \longrightarrow M(H_2O)_x^{n+}(aq) + nNO_3^{-}(aq)$$

If the metal ion, M^{n+} , is small and highly charged, it has a high charge density and withdraws sufficient electron density from the O—H bonds of these bonded water molecules for a proton to be released. That is, the hydrated cation, $M(H_2O)_x^{n+}$, acts as a typical Brønsted-Lowry acid. In the process, the bound H_2O molecule that releases the proton becomes a bound OH^- ion:

$$M(H_2O)_x^{n+}(aq) + H_2O(l) \implies M(H_2O)_{x-1}OH^{(n-1)+}(aq) + H_3O^+(aq)$$

Each type of hydrated metal ion that releases a proton has a characteristic K_a value. Table 18.7 shows some common examples (also see Appendix C).

Aluminum ion, for example, has the small size and high positive charge needed to produce an acidic solution. When an aluminum salt, such as Al(NO₃)₃, dissolves in water, the following steps occur:

$$Al(NO_3)_3(s) + 6H_2O(l) \longrightarrow Al(H_2O)_6^{3+}(aq) + 3NO_3^{-}(aq)$$

[dissolution and hydration]

$$Al(H_2O)_6^{3+}(aq) + H_2O(l) \implies Al(H_2O)_5OH^{2+}(aq) + H_3O^+(aq)$$

[dissociation of weak acid]

Note the formulas of the hydrated metal ions in the last step. When H^+ is released, the number of bound H_2O molecules decreases by 1 (from 6 to 5) and the number of bound OH^- ions increases by 1 (from 0 to 1), which reduces the ion's positive charge by 1 (from 3 to 2) (Figure 18.13).

Through its ability to withdraw electron density from the O—H bonds of the bonded water molecules, a small, highly charged central metal ion behaves like a central electronegative atom in an oxoacid. Salts of most M²⁺ and M³⁺ ions yield acidic aqueous solutions.

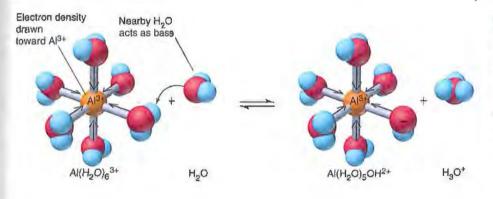


Figure 18.13 The acidic behavior of the hydrated Al³⁺ ion. When a metal ion enters water, it is hydrated as water molecules bond to it. If the ion is small and multiply charged, as is the Al³⁺ ion, it pulls sufficient electron density from the O—H bonds of the attached water molecules to make the bonds more polar, and an H⁺ ion is transferred to a nearby water molecule.

SECTION SUMMARY

The strength of an acid depends on the ease with which the ionizable proton is released. For nonmetal hydrides, acid strength increases across a period, with the electronegativity of the nonmetal (E), and down a group, with the length of the E—H bond. For oxoacids with the same number of O atoms, acid strength increases with electronegativity of E; for oxoacids with the same E, acid strength increases with number of O atoms. Small, highly charged metal ions are acidic in water because they withdraw electron density from the O—H bonds of bound $\rm H_2O$ molecules, releasing an $\rm H^+$ ion to the solution.

Chapter 18 Acid-Base Equilibria

18.7 ACID-BASE PROPERTIES OF SALT SOLUTIONS

Up to now you've seen that cations of weak bases (such as NH₄⁺) are acidic, anions of weak acids (such as CN⁻) are basic, anions of polyprotic acids (such as H₂PO₄⁻) are often acidic, and small, highly charged metal cations (such as Al³⁺) are acidic. Therefore, when salts containing these ions dissolve in water, the pH of the solution is affected. You can predict the relative acidity of a salt solution from the relative ability of the cation and/or anion to react with water. Let's examine the ionic makeup of salts that yield neutral, acidic, or basic solutions to see how we make this prediction.

Salts That Yield Neutral Solutions

A salt consisting of the anion of a strong acid and the cation of a strong base yields a neutral solution because the ions do not react with water. In order to see why the ions don't react, let's consider the dissociation of the parent acid and base. When a strong acid such as HNO₃ dissolves, complete dissociation takes place:

$$HNO_3(l) + H_2O(l) \longrightarrow NO_3^-(aq) + H_3O^+(aq)$$

 $\rm H_2O$ is a much stronger base than $\rm NO_3^-$, so the reaction proceeds essentially to completion. The same argument can be made for any strong acid: the anion of a strong acid is a much weaker base than water. Therefore, a strong acid anion is hydrated, but nothing further happens.

Now consider the dissociation of a strong base, such as NaOH:

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

The Na⁺ ion has a relatively large size and low charge and therefore does not bond strongly with the water molecules around it. When Na⁺ enters water, it becomes hydrated but nothing further happens. The cations of all strong bases behave this way.

The anions of strong acids are the halide ions, except F^- , and those of strong oxoacids, such as NO_3^- and ClO_4^- . The cations of strong bases are those from Group 1A(1) and Ca^{2+} , Sr^{2+} , and Ba^{2+} from Group 2A(2). Salts containing only these ions, such as NaCl and $Ba(NO_3)_2$, yield neutral solutions because no reaction with water takes place.

Salts That Yield Acidic Solutions

A salt consisting of the anion of a strong acid and the cation of a weak base yields an acidic solution because the cation acts as a weak acid, and the anion does not react. For example, NH₄Cl produces an acidic solution because the NH₄⁺ ion, the cation that forms from the weak base NH₃, is a weak acid, and the Cl⁻ ion, the anion of a strong acid, does not react:

$$NH_4Cl(s) \xrightarrow{H_2O} NH_4^+(aq) + Cl^-(aq)$$
 [dissolution and hydration]
 $NH_4^+(aq) + H_2O(l) \Longrightarrow NH_3(aq) + H_3O^+(aq)$ [dissociation of weak acid]

As you saw earlier, *small*, *highly charged metal ions* make up another group of cations that yield H₃O⁺ in solution. For example, Fe(NO₃)₃ produces an acidic solution because the hydrated Fe³⁺ ion acts as a weak acid, whereas the NO₃⁻ ion, the anion of a strong acid, does not react:

$$Fe(NO_3)_3(s) + 6H_2O(l) \xrightarrow{H_2O} Fe(H_2O)_6^{3+}(aq) + 3NO_3^{-}(aq)$$

[dissolution and hydration]

$$Fe(H_2O)_6^{3+}(aq) + H_2O(l) \Longrightarrow Fe(H_2O)_5OH^{2+}(aq) + H_3O^+(aq)$$

[dissociation of weak acid]

A third group of salts that yield H_3O^+ ions in solutions consists of cations of strong bases and anions of polyprotic acids that still have one or more ionizable protons. For example, NaH_2PO_4 yields an acidic solution because Na^+ , the cation of a strong base, does not react, while $H_2PO_4^-$, the first anion of the weak polyprotic acid H_3PO_4 , is also a weak acid:

$$NaH_2PO_4(s) \xrightarrow{H_2O} Na^+(aq) + H_2PO_4^-(aq)$$
 [dissolution and hydration] $H_2PO_4^-(aq) + H_2O(l) \Longrightarrow HPO_4^{2-}(aq) + H_3O^+(aq)$ [dissociation of weak acid]

Salts That Yield Basic Solutions

A salt consisting of the anion of a weak acid and the cation of a strong base yields a basic solution in water because the anion acts as a weak base, and the cation does not react. The anion of a weak acid accepts a proton from water to yield OH⁻ ion. Sodium acetate, for example, yields a basic solution because the Na⁺ ion, the cation of a strong base, does not react with water, and the CH₃COO⁻ ion, the anion of the weak acid CH₃COOH, acts as a weak base:

 $CH_3COONa(s) \xrightarrow{H_2O} Na^+(aq) + CH_3COO^-(aq)$ [dissolution and hydration] $CH_3COO^-(aq) + H_2O(l) \Longrightarrow CH_3COOH(aq) + OH^-(aq)$ [reaction of weak base]

Table 18.8 displays the acid-base behavior of the various types of salts in water.

| Salt Solution (Examples) | рН | Nature of Ions | Ion That Reacts with Water | |
|---|------|---|-------------------------------|----------|
| Neutral [NaCl, KBr, Ba(NO ₃) ₂] | 7.0 | Cation of strong base Anion of strong acid | None | |
| Acidic (NH ₄ Cl, NH ₄ NO ₃ , CH ₃ NH ₃ Br) | <7.0 | Cation of weak base Anion of strong acid | Cation | |
| Acidic [Al(NO ₃) ₃ , CrCl ₃ , FeBr ₃] | <7.0 | Small, highly charged cation Anion of strong acid | Cation | |
| Acidic (NaH ₂ PO ₄ , KHSO ₄ , NaHSO ₃) | <7.0 | Cation of strong base First anion of polyprotic acid | Anion | |
| Basic (CH ₃ COONa, KF, Na ₂ CO ₃) | >7.0 | Cation of strong base Anion of weak acid | Anion | ND I I I |

Chapter 18 Acid-Base Equilibria

SAMPLE PROBLEM 18.11 Predicting Relative Acidity of Salt Solutions

Problem Predict whether aqueous solutions of the following are acidic, basic, or neutral, and write an equation for the reaction of any ion with water:

(a) Potassium perchlorate, KClO₄

(b) Sodium benzoate, C₆H₅COONa

(c) Chromium trichloride, CrCl₃

(d) Sodium hydrogen sulfate, NaHSO4

Plan We examine the formulas to determine the cations and anions. Depending on the nature of these ions, the solution will be neutral (strong-acid anion and strong-base cation), acidic (weak-base cation and strong-acid anion, highly charged metal cation, or first anion of a polyprotic acid), or basic (weak-acid anion and strong-base cation).

Solution (a) Neutral. The ions are K^+ and ClO_4^- . The K^+ ion is from the strong base KOH, and the ClO_4^- anion is from the strong acid $HClO_4$. Neither ion reacts with water, (b) Basic. The ions are Na^+ and $C_6H_5COO^-$. Na^+ is the cation of the strong base NaOH and does not react with water. The benzoate ion, $C_6H_5COO^-$, is from the weak acid benzoic acid, so it reacts with water to produce OH^- ion:

$$C_6H_5COO^-(aq) + H_2O(l) \Longrightarrow C_6H_5COOH(aq) + OH^-(aq)$$

(c) Acidic. The ions are Cr^{3+} and Cl^- . Cl^- is the anion of the strong acid HCl, so it does not react with water. Cr^{3+} is a small metal ion with a high positive charge, so the hydrated ion, $Cr(H_2O)_6^{3+}$, reacts with water to produce H_3O^+ :

$$Cr(H_2O)_6^{3+}(aq) + H_2O(l) \implies Cr(H_2O)_5OH^{2+}(aq) + H_3O^+(aq)$$

(d) Acidic. The ions are Na⁺ and HSO_4^- . Na⁺ is the cation of the strong base NaOH, so it does not react with water. HSO_4^- is the first anion of the diprotic acid H_2SO_4 , and it reacts with water to produce H_3O^+ :

$$HSO_4^-(aq) + H_2O(l) \implies SO_4^{2-}(aq) + H_3O^+(aq)$$

FOLLOW-UP PROBLEM 18.11 Write equations to predict whether solutions of the following salts are acidic, basic, or neutral: (a) KClO₂; (b) CH₃NH₃NO₃; (c) CsI.

Salts of Weakly Acidic Cations and Weakly Basic Anions

The only salts left to consider are those consisting of a cation that acts as a weak acid and an anion that acts as a weak base. In these cases, and there are quite a few, both ions react with water. It makes sense, then, that the overall acidity of the solution will depend on the relative acid strength or base strength of the separated ions, which can be determined by comparing their equilibrium constants.

For example, will an aqueous solution of ammonium hydrogen sulfide, NH₄HS, be acidic or basic? First, we write equations for any reactions that occur between the separated ions and water. Ammonium ion is the conjugate acid of a weak base, so it acts as a weak acid:

$$NH_4^+(aq) + H_2O(l) \implies NH_3(aq) + H_3O^+(aq)$$

Hydrogen sulfide ion is the anion of the weak acid H2S, so it acts as a weak base:

$$HS^-(aq) + H_2O(l) \Longrightarrow H_2S(aq) + OH^-(aq)$$

The reaction that goes farther to the right will have the greater influence on the pH of the solution, so we must compare the K_a of $\mathrm{NH_4}^+$ with the K_b of HS⁻. Recall that only molecular compounds are listed in K_a and K_b tables, so we have to calculate these values for the ions:

$$K_{\rm u} \text{ of NH}_4^+ = \frac{K_{\rm w}}{K_{\rm b} \text{ of NH}_3} = \frac{1.0 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.7 \times 10^{-10}$$

$$K_{\rm b} \text{ of HS}^- = \frac{K_{\rm w}}{K_{\rm n1} \text{ of H}_2 \text{S}} = \frac{1.0 \times 10^{-14}}{9 \times 10^{-8}} = 1 \times 10^{-7}$$

The difference in magnitude of the equilibrium constants ($K_b \approx 200K_a$) tells us that the acceptance of a proton from H_2O by HS^- proceeds further than the donation of a proton to H_2O by NH_4^+ . In other words, because K_b of $HS^- > K_a$ of NH_4^+ , the NH_4HS solution is basic.

SAMPLE PROBLEM 18.12 Predicting the Relative Acidity of a Salt Solution from K_a and K_b of the Ions

Problem Determine whether an aqueous solution of zinc formate, Zn(HCOO)₂, is acidic, basic, or neutral.

Plan The formula consists of the small, highly charged, and therefore weakly acidic, Zn^{2+} cation and the weakly basic HCOO⁻ anion of the weak acid HCOOH. To determine the relative acidity of the solution, we write equations that show the reactions of the ions with water, and then find K_a of Zn^{2+} (from Appendix C) and calculate K_b of HCOO⁻ (from K_a of HCOOH in Appendix C) to see which ion reacts to a greater extent.

$$Zn(H_2O)_6^{2+}(aq) + H_2O(l) \Longrightarrow Zn(H_2O)_5OH^+(aq) + H_3O^+(aq)$$

 $HCOO^-(aq) + H_2O(l) \Longrightarrow HCOOH(aq) + OH^-(aq)$

Obtaining K_a and K_b of the ions: The K_a of $Zn(H_2O)_6^{2+}(aq)$ is 1×10^{-9} . We obtain K_a of HCOOH and solve for K_b of HCOO⁻:

$$K_{\rm b}$$
 of HCOO⁻ = $\frac{K_{\rm w}}{K_{\rm a}$ of HCOOH = $\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}}$ = 5.6×10⁻¹¹

 $K_{\rm a}$ of ${\rm Zn}({\rm H_2O)_6}^{2+} > K_{\rm b}$ of HCOO⁻, so the solution is acidic.

FOLLOW-UP PROBLEM 18.12 Determine whether solutions of the following salts are acidic, basic, or neutral: (a) Cu(CH₃COO)₂; (b) NH₄F.

SECTION SUMMARY

Salts that yield a neutral solution consist of ions that do not react with water. Salts that yield an acidic solution contain an unreactive anion and a cation that releases a proton to water. Salts that yield a basic solution contain an unreactive cation and an anion that accepts a proton from water. If both cation and anion react with water, the ion that reacts to the greater extent (higher K) determines the acidity or basicity of the salt solution.

18.8 GENERALIZING THE BRØNSTED-LOWRY CONCEPT: THE LEVELING EFFECT

We conclude our focus on the Brønsted-Lowry concept with an important principle that holds for acid-base behavior in any solvent. Notice that, in $\rm H_2O$, all Brønsted-Lowry acids yield $\rm H_3O^+$ and all Brønsted-Lowry bases yield $\rm OH^-$ —the ions that form when the solvent autoionizes. In general, an acid yields the cation and a base yields the anion of solvent autoionization.

This idea lets us examine a question you may have been wondering about: why are all strong acids and strong bases equally strong in water? The answer is that in water, the strongest acid possible is H_3O^+ and the strongest base possible is OH^- . The moment we put some gaseous HCl in water, it reacts with the base H_2O and forms H_3O^+ . The same holds for HNO₃, H_2SO_4 , and any strong acid. All strong acids are equally strong in water because they dissociate completely to form H_3O^+ . Given that the strong acid is no longer present, we are actually observing the acid strength of H_3O^+ .

Chapter 18 Acid-Base Equilibria

Similarly, strong bases, such as $Ba(OH)_2$, dissociate completely in water to yield OH^- . Even those that do not contain hydroxide ions in the solid, such as K_2O , do so. The oxide ion, which is a stronger base than OH^- , immediately takes a proton from water to form OH^- :

$$2K^{+}(aq) + O^{2-}(aq) + H_2O(l) \longrightarrow 2K^{+}(aq) + 2OH^{-}(aq)$$

No matter what species we try, any acid stronger than H_3O^+ simply donates its proton to H_2O , and any base stronger than OH^- accepts a proton from H_2O . Thus, water exerts a **leveling effect** on any strong acid or base by reacting with it to form the products of water's autoionization. Acting as a base, water levels the strength of all strong acids by making them appear equally strong, and acting as an acid, it levels the strength of all strong bases as well.

To rank strong acids in terms of relative strength, we must dissolve them in a solvent that is a *weaker* base than water, one that accepts their protons less readily. For example, you saw in Figure 18.11 that the hydrohalic acids increase in strength as the halogen becomes larger, as a result of the longer, weaker H—X bond. In water, HF is weaker than the other hydrogen halides, but HCl, HBr, and HI appear equally strong because water causes them to dissociate completely. When we dissolve them in pure acetic acid, however, the acetic acid acts as the base and accepts a proton from the acids:

$$\begin{array}{c} \text{acid} & \text{base} & \text{acid} \\ \text{HCl}(g) + \text{CH}_3\text{COOH}(l) & \rightleftharpoons \text{Cl}^-(acet) + \text{CH}_3\text{COOH}_2^+(acet) \\ \text{HBr}(g) + \text{CH}_3\text{COOH}(l) & \rightleftharpoons \text{Br}^-(acet) + \text{CH}_3\text{COOH}_2^+(acet) \\ \text{HI}(g) + \text{CH}_3\text{COOH}(l) & \rightleftharpoons \text{I}^-(acet) + \text{CH}_3\text{COOH}_2^+(acet) \end{array}$$

[The use of (acet) instead of (aq) indicates solvation by CH₃COOH.] However, because acetic acid is a weaker base than water, the three acids protonate it to different extents. Measurements show that HI protonates the solvent to a greater extent than HBr, and HBr does so more than HCl; that is, in pure acetic acid, $K_{\rm HI} > K_{\rm HBr} > K_{\rm HCl}$. Therefore, HCl is a weaker acid than HBr, which is weaker than HI. Similarly, the relative strength of strong bases is determined in a solvent that is a weaker acid than H₂O, such as liquid NH₃.

SECTION SUMMARY

Strong acids (or strong bases) dissociate completely to yield H_3O^+ (or OH^-) in water; in effect, water equalizes (levels) their strengths. Acids that are equally strong in water show differences in strength when dissolved in a solvent that is a weaker base than water, such as acetic acid.

18.9 ELECTRON-PAIR DONATION AND THE LEWIS ACID-BASE DEFINITION

The final acid-base concept we consider was developed by Gilbert N. Lewis, whose contribution to understanding the importance of valence electron pairs in molecular bonding we discussed in Chapter 9. Whereas the Brønsted-Lowry concept focuses on the proton in defining a species as an acid or a base, the Lewis concept highlights the role of the electron pair. The Lewis acid-base definition holds that

- A base is any species that donates an electron pair.
- An acid is any species that accepts an electron pair.

The Lewis definition, like the Brønsted-Lowry definition, requires that a base have an electron pair to donate, so it does not expand the classes of bases. However, it greatly expands the classes of acids. Many species, such as CO₂ and Cu²⁺, that do not contain H in their formula (and thus cannot be Brønsted-Lowry acids)

$$B + H^+ \Longrightarrow B - H^+$$

Thus, all Brønsted-Lowry acids donate H⁺, a Lewis acid.

The product of any Lewis acid-base reaction is called an adduct, a single species that contains a new covalent bond:

$$A + B \implies A - B$$
 (adduct)

Thus, the Lewis concept radically broadens the idea of acid-base reactions. What to Arrhenius was the formation of H_2O from H^+ and OH^- became, to Brønsted and Lowry, the transfer of a proton from a stronger acid to a stronger base to form a weaker base and weaker acid. To Lewis, the same process became the donation and acceptance of an electron pair to form a covalent bond in an adduct.

As we've seen, the key feature of a Lewis base is a lone pair of electrons to donate. The key feature of a Lewis acid is a vacant orbital (or the ability to rearrange its bonds to form one) to accept that lone pair and form a new bond. There are a variety of neutral molecules and positively charged ions that satisfy this requirement.

Molecules as Lewis Acids

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Many neutral molecules function as Lewis acids. In every case, the atom that accepts the electron pair is low in electron density because of either an electron deficiency or a polar multiple bond.

Lewis Acids with Electron-Deficient Atoms Some molecular Lewis acids contain a central atom that is *electron deficient*, one surrounded by fewer than eight valence electrons. The most important are covalent compounds of the Group 3A(13) elements boron and aluminum. As noted in Chapters 10 and 14, these compounds react vigorously to complete their octet. For example, boron trifluoride accepts an electron pair from ammonia to form a covalent bond in a gaseous Lewis acid-base reaction:

Unexpected solubility behavior is sometimes due to adduct formation. Aluminum chloride, for instance, dissolves freely in relatively nonpolar diethyl ether because of a Lewis acid-base reaction, in which the ether's O atom donates an electron pair to Al to form a covalent bond:

$$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \ddot{\bigcirc} : + \text{A} \\ \text{CH}_3 - \text{CH}_2 - \ddot{\bigcirc} : + \text{A} \\ \text{CH}_3 - \text{CH}_2 - \ddot{\bigcirc} : + \text{CH}_3 - \text{CH}_2 - \ddot{\bigcirc} : \\ \text{CH}_3 - \text{CH}_2 : \dot{\bigcirc} : \\ \text{Dase} \\ \text{acid} \\ \end{array}$$

This acidic behavior of boron and aluminum halides is put to use in many organic syntheses. For example, toluene, an important solvent and organic reagent, can be made by the action of CH₃Cl on benzene in the presence of AlCl₃. The

Chapter 18 Acid-Base Equilibria

Lewis acid AlCl₃ abstracts the Lewis base Cl⁻ from CH₃Cl to form an adduct that has a reactive CH₃⁺ group, which attacks the benzene ring:

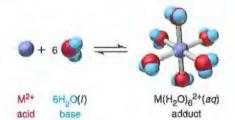
Lewis Acids with Polar Multiple Bonds Molecules that contain a polar double bond also function as Lewis acids. As the electron pair on the Lewis base approaches the partially positive end of the double bond, one of the bonds breaks to form the new bond in the adduct. For example, consider the reaction that occurs when SO_2 dissolves in water. The electronegative O atoms in SO_2 withdraw electron density from the central S, so it is partially positive. The O atom of water donates a lone pair to the S, breaking one of the π bonds and forming an S—O bond, and a proton is transferred from water to that O. The resulting adduct is sulfurous acid, and the overall process is

The formation of carbonates from a metal oxide and carbon dioxide is an analogous reaction that occurs in a nonaqueous heterogeneous system. The O^{2-} ion (shown below from CaO) donates an electron pair to the partially positive C in CO_2 , a π bond breaks, and the CO_3^{2-} ion forms as the adduct:

$$Ca^{2+}: \ddot{O}: \overset{?}{\longrightarrow} + : \ddot{O} = \overset{?}{\bigcirc} = \overset{?}{\bigcirc}: \qquad \qquad Ca^{2+} = \begin{bmatrix} :O: \\ :$$

Metal Cations as Lewis Acids

Earlier we saw that certain hydrated metal ions act as Brønsted-Lowry acids. In the Lewis sense, the hydration process itself is an acid-base reaction. The hydrated cation is the adduct, as lone electron pairs on the O atoms of water form covalent bonds to the positively charged ion; thus, any metal ion acts as a Lewis acid when it dissolves in water:



Ammonia is a stronger Lewis base than water because it displaces H_2O from a hydrated ion when aqueous NH_3 is added:

$$Ni(H_2O)_6^{2+}(aq) + 6NH_3(aq) \implies Ni(NH_3)_6^{2+}(aq) + 6H_2O(l)$$

hydrated adduct base Ni(NH_3)6

We discuss the equilibrium nature of these acid-base reactions in greater detail in Chapter 19, and we investigate the structures of these ions in Chapter 23.

Many biomolecules are Lewis adducts with central metal ions. Most often, O and N atoms of organic groups, with their lone pairs, serve as the Lewis bases.

Chlorophyll is a Lewis adduct of a central Mg2+ ion and the four N atoms of an organic tetrapyrrole ring system (Figure 18.14). Vitamin B₁₂ has a similar structure with a central Co³⁺, and so does heme, but with a central Fe²⁺. Several other metal ions, such as Zn²⁺, Mo²⁺, and Cu²⁺, are bound at the active sites of enzymes and function as Lewis acids in the catalytic action.

SAMPLE PROBLEM 18.13 Identifying Lewis Acids and Bases

Problem Identify the Lewis acids and Lewis bases in the following reactions:

(a) $H^+ + OH^- \Longrightarrow H_2O$ (b) $Cl^- + BCl_3 \Longrightarrow BCl_4^-$ (c) $K^+ + 6H_2O \Longrightarrow K(H_2O)_6^+$

Plan We examine the formulas to see which species accepts the electron pair (Lewis acid) and which donates it (Lewis base) in forming the adduct.

Solution (a) The H⁺ ion accepts an electron pair from the OH⁻ ion in forming a bond. H⁺ is the acid and OH⁻ is the base.

(b) The Cl ion has four lone pairs and uses one to form a new bond to the central B. Therefore, BCl₃ is the acid and Cl⁻ is the base.

(c) The K+ ion does not have any valence electrons to provide, so the bond is formed when electron pairs from O atoms of water enter empty orbitals on K+. Thus, K⁺ is the acid and H₂O is the base.

check The Lewis acids (H+, BCl3, and K+) each have an unfilled valence shell that can accept an electron pair from the Lewis bases (OH-, Cl-, and H2O).

FOLLOW-UP PROBLEM 18.13 Identify the Lewis acids and Lewis bases in the following reactions:

(a) OH[−] + Al(OH)₃ ⇒ Al(OH)₄[−]

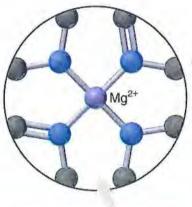
(b) $SO_3 + H_2O \implies H_2SO_4$ (c) $Co^{3+} + 6NH_3 \implies Co(NH_3)_6^{3+}$

An Overview of Acid-Base Definitions

By looking closely at the essential chemical change involved, chemists can see a common theme in reactions as diverse as a standardized base being used to analyze an unknown fatty acid, baking soda being used in breadmaking, and even oxygen binding to hemoglobin in a blood cell. From this wider perspective, the diversity of acid-base reactions takes on more unity. Let's stand back and survey the scope of the three acid-base definitions and see how they fit together.

The classical (Arrhenius) definition, which was the first attempt at describing acids and bases on the molecular level, is the most limited and narrow of the three definitions. It applies only to species whose structures include an H atom or an OH group that is released as an ion when the species dissolves in water. Because relatively few species have these prerequisites, Arrhenius acid-base reactions are relatively few in number, and all such reactions result in the formation of H2O.

The Brønsted-Lowry definition is more general, seeing acid-base reactions as proton-transfer processes and eliminating the requirement that they occur in water. Whereas a Brønsted-Lowry acid, like an Arrhenius acid, still must have an H, a Brønsted-Lowry base is defined as any species with an electron pair available to accept a transferred proton. This definition includes a great many more species as bases. Furthermore, it defines the acid-base reaction in terms of conjugate acidbase pairs, with an acid and a base on both sides of the reaction. The system reaches an equilibrium state based on the relative strengths of the acid, the base, and their conjugates.



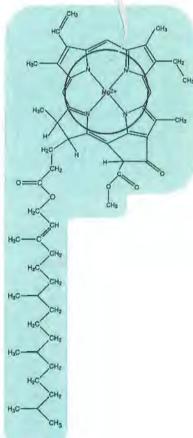


Figure 18.14 The Mg2+ ion as a Lewis acid in the chlorophyll molecule. Many biomolecules contain metal ions that act as Lewis acids. In chlorophyll, Mg2+ accepts electron pairs from surrounding N atoms that are part of the large organic portion of the molecule.

Chapter 18 Acid-Base Equilibria

The Lewis definition has the widest scope of the three. The defining event of a Lewis acid-base reaction is the donation and acceptance of an electron pair to form a new covalent bond. Lewis bases still must have an electron pair to donate, but Lewis acids—as electron-pair acceptors—include many species not encompassed by the other two definitions, including molecules with electron-deficient atoms or with polar double bonds, metal ions, and the proton itself.

SECTION SUMMARY

The Lewis acid-base definition focuses on the donation or acceptance of an electron pair to form a new covalent bond in an adduct, the product of an acid-base reaction. Lewis bases donate the electron pair, and Lewis acids accept it. Thus, many species that do not contain H are Lewis acids. Molecules with polar double bonds act as Lewis acids, as do those with electron-deficient atoms. Metal ions act as Lewis acids when they dissolve in water, which acts as a Lewis base, to form the adduct, a hydrated cation. Many metal ions function as Lewis acids in biomolecules.

Chapter Perspective

In this chapter, we extended the principles of equilibrium to acids and bases. We also investigated one direction in which the science of chemistry matured, as narrow definitions of acids and bases progressively widened to encompass different species, physical states, solvent systems, and reaction types. Acids and bases, by whatever definition, are an extremely important group of substances. In Chapter 19, we continue our discussion of acid-base behavior and apply many of the ideas developed here to other aqueous equilibria.

For Review and Reference (Numbers in parentheses refer to pages, unless noted otherwise.)

Learning Objectives

Relevant section and/or sample problem (SP) numbers appear in parentheses.

Understand These Concepts

- 1. Why the proton is bonded to a water molecule, as H_3O^+ , in all aqueous acid-base systems (Section 18.1)
- 2. The classical (Arrhenius) definitions of an acid and a base (Section 18.1)
- 3. Why all reactions of a strong acid and a strong base have the same $\Delta H_{\rm rxn}^0$ (Section 18.1)
- How the strength of an acid (or base) relates to the extent of its dissociation into ions in water (Section 18.1)
- 5. How relative acid strength is expressed by the acid-dissociation constant K_a (Section 18.1)
- 6. Why water is a very weak electrolyte and how its autoionization is expressed by $K_{\rm w}$ (Section 18.2)
- 7. Why $[H_3O^+]$ is inversely related to $[OH^-]$ in any aqueous solution (Section 18.2)
- 8. How the relative magnitudes of [H₃O⁺] and [OH⁻] define whether a solution is acidic, basic, or neutral (Section 18.2)
- The Brønsted-Lowry definitions of an acid and a base and how an acid-base reaction can be viewed as a proton-transfer process (Section 18.3)
- 10. How water acts as a base (or as an acid) when an acid (or a base) dissolves in it (Section 18.3)
- 11. How a conjugate acid-base pair differs by one proton (Section 18.3)
- 12. How a Brønsted-Lowry acid-base reaction involves two conjugate acid-base pairs (Section 18.3)

- 13. Why a stronger acid and base react $(K_c > 1)$ to form a weaker base and acid (Section 18.3)
- 14. How percent dissociation of a weak acid increases as its concentration decreases (Section 18.4)
- 15. How a polyprotic acid dissociates in two or more steps and why only the first step supplies significant [H₃O⁺] (Section 18.4)
- 16. How weak bases in water accept a proton rather than dissociate; the meaning of K_b and pK_b (Section 18.5)
- 17. How ammonia, amines, and weak-acid anions act as weak bases in water (Section 18.5)
- 18. Why relative concentrations of HA and A determine the acidity or basicity of their solution (Section 18.5)
- 19. The relationship of the K_a and K_b of a conjugate acid-base pair to K_w (Section 18.5)
- 20. The effects of electronegativity, bond polarity, and bond strength on acid strength (Section 18.6)
- 21. Why aqueous solutions of small, highly charged metal ions are acidic (Section 18.6)
- 22. The various combinations of cations and anions that lead to acidic, basic, or neutral salt solutions (Section 18.7)
- 23. Why the strengths of strong acids are leveled in water but differentiated in a less basic solvent (Section 18.8)
- 24. The Lewis definitions of an acid and a base and how a Lewis acid-base reaction involves the donation and acceptance of an electron pair to form a covalent bond (Section 18.9)
- How molecules with electron-deficient atoms or polar multiple bonds and metal cations act as Lewis acids (Section 18.9)

For Review and Reference

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Master These Skills

- 1. Classifying strong and weak acids and bases from their formulas (SP 18.1)
- 2. Using K_w to calculate $[H_3O^+]$ and $[OH^-]$ in an aqueous solution (SP 18.2)
- 3. Using p-scales to express [H₃O⁺], [OH⁻], and K (Section 18.2)
- 4. Calculating [H₃O⁺], pH, [OH⁻], and pOH (SP 18.3)
- 5. Identifying conjugate acid-base pairs (SP 18.4)
- 6. Using relative acid strengths to predict the net direction of an acid-base reaction (SP 18.5)
- 7. Calculating K_a of a weak acid from pH (SP 18.6)
- 8. Calculating $[H_3O^+]$ (and, thus, pH) from K_a and $[HA]_{init}$ (SP 18.7)

- 9. Applying the quadratic equation to find a concentration (Follow-up Problem 18.7)
- 10. Calculating the percent dissociation of a weak acid (Section 18.4)
- 11. Calculating [H₃O⁺] and other concentrations for a polyprotic acid (SP 18.8)
- 12. Calculating pH from K_b and [B]_{init} (SP 18.9)
- 13. Finding K_b of A from K_a of HA and K_w (Section 18.5 and SP 18.10)
- 14. Calculating pH from Kb of A and [A]init (SP 18.10)
- 15. Predicting relative acid strengths of nonmetal hydrides and oxoacids (Section 18.6)
- 16. Predicting the relative acidity of a salt solution from the nature of the cation and anion (SPs 18.11 and 18.12)
- 17. Identifying Lewis acids and bases (SP 18.13)

Key Terms

Section 18.1

(770)

hydronium ion, H₃O⁺ (768) classical (Arrhenius) acid-base definition (768) neutralization (768) acid-dissociation (acidionization) constant (K_a)

Section 18.2

autoionization (773)
ion-product constant for water
(K_w) (773)
pH (775)
acid-base indicator (777)

Section 18.3

Brønsted-Lowry acid-base definition (777)

proton donor (777) proton acceptor (778) conjugate acid-base pair (779)

Section 18.4

polyprotic acid (786)

Section 18.5

base-dissociation (baseionization) constant (K_b) (788) Section 18.8

leveling effect (800)

Section 18.9

Lewis acid-base definition (800) adduct (801)

Key Equations and Relationships

18.1 Defining the acid-dissociation constant (770):

$$K_{a} = \frac{[\mathrm{H}_{3}\mathrm{O}^{+}][\mathrm{A}^{-}]}{[\mathrm{H}\mathrm{A}]}$$

18.2 Defining the ion-product constant for water (773):

$$K_{\rm w} = [{\rm H_3O}^+][{\rm OH}^-] = 1.0 \times 10^{-14} \,({\rm at}\,25^{\circ}{\rm C})$$

18.3 Defining pH (775):

$$pH = -\log [H_3O^+]$$

18.4 Relating pK_w to pH and pOH (776):

$$pK_w = pH + pOH = 14.00 \text{ (at 25°C)}$$

18.5 Finding the percent dissociation of HA (785):

Percent HA dissociated =
$$\frac{[HA]_{dissoc}}{[HA]_{init}} \times 100$$

18.6 Defining the base-dissociation constant (788):

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

18.7 Expressing the relationship among K_a , K_b , and K_w (792):

$$K_{\rm a} \times K_{\rm b} = K_{\rm w}$$

Highlighted Figures and Tables

These figures (F) and tables (T) provide a review of key ideas. Entries in color contain frequently used data.

F18.1 Extent of dissociation for strong acids (769)

F18.2 Extent of dissociation for weak acids (770)

F18.4 Defining acidic, neutral, and basic solutions (774)

F18.6 Relations among [H₃O⁺], pH, [OH⁻], and pOH (776)

F18.8 Proton transfer in Brønsted-Lowry acid-base reactions (778)

T18.4 Some conjugate acid-base pairs (779)

F18.9 Strengths of conjugate acid-base pairs (781)

F18.11 Trends in nonmetal hydride acidity (793)

F18.12 Relative strengths of oxoacids (794)

T18.8 Behavior of salts in water (797)

Chapter 18 Acid-Base Equilibria

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Brief Solutions to Follow-up Problems

18.1 (a) HClO₃; (b) HCl; (c) NaOH
18.2 [H₃O⁺] =
$$\frac{1.0 \times 10^{-14}}{6.7 \times 10^{-2}}$$
 = 1.5×10⁻¹³ M; basic
18.3 pOH = 14.00 - 9.52 = 4.48
[H₃O⁺] = $10^{-9.52}$ = 3.0×10⁻¹⁰ M
[OH⁻] = $\frac{1.0 \times 10^{-14}}{3.0 \times 10^{-10}}$ = 3.3×10⁻⁵ M
18.4 (a) CH₃COOH/CH₃COO⁻ and H₃O⁺/H₂O
(b) H₂O/OH⁻ and HF/F⁻
18.5 (a) NH₃(g) + H₂O(f) \Longrightarrow NH₄⁺(aq) + OH⁻(aq)
(b) NH₃(g) + H₃O⁺(aq; from HCl) \Longrightarrow NH₄⁺(aq) + H₂O(f)
(c) NH₄⁺(aq) + OH⁻(aq; from NaOH) \Longrightarrow NH₃(g) + H₂O(f)
18.6 NH₄⁺(aq) + H₂O(f) \Longrightarrow NH₃(aq) + H₃O⁺(aq)
[H₃O⁺] = $10^{-\text{pH}}$ = $10^{-5.0}$ = 1×10^{-5} M = [NH₃]
From reaction table, $K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{(x)(x)}{0.2 - x}$
 $\approx \frac{(1 \times 10^{-5})^2}{0.2} = 5 \times 10^{-10}$
18.7 $K_a = \frac{[H_3O^+][OCN^-]}{[HOCN]} = \frac{(x)(x)}{0.10 - x} = 3.5 \times 10^{-4}$
Since $\frac{[HOCN]_{\text{init}}}{K_a} = \frac{0.10}{3.5 \times 10^{-4}} = 2.86 < 400$, you must solve a quadratic equation: $x^2 + (3.5 \times 10^{-4})x - (3.5 \times 10^{-5}) = 0$
 $x = [H3O+] = 5.7 \times 10^{-3}$ M; pH = 2.24
18.8 $K_{a1} = \frac{[HC_2O_4^-][H3O^+]}{[H2C2O4]} = \frac{x^2}{0.150 - x} = 5.6 \times 10^{-2}$
Since $\frac{[H_2C_2O_4]_{\text{init}}}{K_{a1}} < 400$, you must solve a quadratic equation: $x^2 + (5.6 \times 10^{-2})x - (8.4 \times 10^{-3}) = 0$
 $x = [H3O+] = 0.068$ M; pH = 1.17
 $x = [HC_2O_4^-] = 0.068$ M; pH = 1.17
 $x = [HC_2O_4^-] = 0.068$ M; pH = 1.17
 $x = [HC_2O_4^-] = 0.068$ M; pH = 1.17
 $x = [HC_2O_4^-] = 0.068$ M; pH = 1.17
 $x = [HC_2O_4^-] = 0.068$ M; [H₂C₂O₄] = 0.150 M - x = 0.082 M
[C₂O₄²⁻] = $\frac{(K_{a2})[HC_2O_4^-]}{[H3O+]} = \frac{(5.4 \times 10^{-5})(0.068)}{0.068}$
= 5.4×10⁻⁵ M

18.9
$$K_b = \frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]} = 10^{-8.77} = 1.7 \times 10^{-9}$$

Assuming $0.10 M - x \approx 0.10 M$, $K_b = 1.7 \times 10^{-9} \approx \frac{(x)(x)}{0.10}$; $x = [OH^-] \approx 1.3 \times 10^{-5} M$; $[H_3O^+] = 7.7 \times 10^{-10} M$; $pH = 9.11$

18.10 K_b of $CIO^- = \frac{K_w}{K_a}$ of $HCIO^- = \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-8}} = 3.4 \times 10^{-7}$

Assuming $0.20 M - x \approx 0.20 M$, $K_b = 3.4 \times 10^{-7} = \frac{[HCIO][OH^-]}{[CIO^-]} \approx \frac{x^2}{0.20}$; $x = [OH^-] \approx 2.6 \times 10^{-4} M$; $[H_3O^+] = 3.8 \times 10^{-11} M$; $pH = 10.42$

18.11 (a) Basic: $CIO_2^-(aq) + H_2O(l) \Longrightarrow HCIO_2(aq) + OH^-(aq)$ K^+ is from strong base KOH. (b) Acidic: $CH_3NH_3^+(aq) + H_2O(l) \Longrightarrow CH_3NH_2(aq) + H_3O^+(aq)$ NO_3^- is from strong acid HNO_3 . (c) Neutral: Cs^+ is from strong base $CsOH$; I^- is from strong acid HI .

18.12 (a) K_a of $Cu(H_2O)_6^{2+} = 3 \times 10^{-8} K_b$ of $CH_3COO^- = \frac{K_w}{K_a}$ of $CH_3COOH^- = 5.6 \times 10^{-10}$ $Since K_a > K_b$, $Cu(CH_3COO)_2(aq)$ is acidic. (b) K_a of $NH_4^+ = \frac{K_w}{K_b}$ of $NH_4^- = \frac{K_w}{$

Problems

Problems with colored numbers are answered in Appendix E. Sections match the text and provide the numbers of relevant sample problems. Most offer Concept Review Questions, Skill-Building Exercises (grouped in pairs covering the same concept), and Problems in Context. Comprehensive Problems are based on material from any section or previous chapter.

Note: Unless stated otherwise, all problems refer to aqueous solutions at 298 K (25°C).

Acids and Bases in Water

(Sample Problem 18.1)

Concept Review Questions

18.1 Describe the role of water according to the classical (Arrhenius) acid-base definition.

18.2 What characteristics do all Arrhenius acids have in common? What characteristics do all Arrhenius bases have in common? Explain neutralization in terms of the Arrhenius acid-base defi-

nition. What quantitative finding led Arrhenius to propose this idea of neutralization?

18.3 Why is the Arrhenius acid-base definition considered too limited? Give an example of a case in which the Arrhenius definition does not apply.

18.4 What is meant by the words "strong" and "weak" in terms of acids and bases? Weak acids have K_a values that vary over more than 10 orders of magnitude. What do they have in common that classifies them as "weak"?

Skill-Building Exercises (grouped in similar pairs)

18.5 Which of the following are Arrhenius acids?

(a) H₂O (b) Ca(OH)₂ (c) H₃PO₃ (d) HI

(c) NH3 is the Lewis base; Co3+ is the Lewis acid.

18.6 Which of the following are Arrhenius acids?

(a) NaHSO₄ (b) CH₄ (c) NaH (d) H₃N

18.7 Which of the following are Arrhenius bases?

(a) H₃AsO₄ (b) Ba(OH)₂ (c) HClO (d) KOH

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18.8 Which of the following are Arrhenius bases?

(a) CH₃COOH (b) HOH (c) CH₃OH (d) H₂NNH₂

18.9 Write the K_a expression for each of the following in water: (a) HCN (b) HCO₃ (c) HCOOH

18.10 Write the K_n expression for each of the following in water: (a) $CH_3NH_3^+$ (b) HCIO (c) H_2S

18.11 Write the K_a expression for each of the following in water: (a) HNO₂ (b) CH₃COOH (c) HBrO₂

18.12 Write the K_a expression for each of the following in water: (a) H_2PO_4 (b) H_3PO_2 (c) HSO_4

18.13 Use Appendix C to rank the following in order of increasing acid strength: HIO₃, HI, CH₃COOH, HF.

18.14 Use Appendix C to rank the following in order of decreasing acid strength: HClO, HCl, HCN, HNO₂.

18.15 Classify each as a strong or weak acid or base:

(a) H₃AsO₄ (b) Sr(OH)₂ (c) HIO (d) HClO₄

18.16 Classify each as a strong or weak acid or base:

(a) CH₃NH₂ (b) K₂O (c) HI (d) HCOOH

18.17 Classify each as a strong or weak acid or base:

(a) RbOH (b) HBr (c) H₂Te (d) HClO

18.18 Classify each as a strong or weak acid or base:

(a) HOCH₂CH₂NH₂ (b) H₂SeO₄ (c) HS⁻ (d) B(OH)₃

Autoionization of Water and the pH Scale

(Sample Problems 18.2 and 18.3)

Concept Review Questions

18.19 What is an autoionization reaction? Write equations for the autoionization reactions of H₂O and of H₂SO₄.

18.20 What is the difference between K_c and K_w for the auto-ionization of water?

18.21 (a) What is the change in pH when [OH⁻] increases by a factor of 10?

(b) What is the change in $[H_3O^+]$ when the pH decreases by 2 units?

18.22 Which solution has the higher pH? Explain.

(a) A 0.1 M solution of an acid with $K_a = 1 \times 10^{-4}$ or one with $K_a = 4 \times 10^{-5}$

(b) A 0.1 M solution of an acid with $pK_a = 3.0$ or one with $pK_a = 3.5$

(c) A 0.1 M solution of a weak acid or a 0.01 M solution of the same acid

(d) A 0.1 M solution of a weak acid or a 0.1 M solution of a strong acid

(e) A 0.1 M solution of an acid or a 0.1 M solution of a base

(f) A solution of pOH 6.0 or one of pOH 8.0

Skill-Building Exercises (grouped in similar pairs)

18.23 (a) What is the pH of 0.0111 M NaOH? Is the solution neutral, acidic, or basic?

(b) What is the pOH of 1.23×10^{-3} M HCl? Is the solution neutral, acidic, or basic?

18.24 (a) What is the pH of 0.0333 M HNO₃? Is the solution neutral, acidic, or basic?

(b) What is the pOH of 0.0347 M KOH? Is the solution neutral, acidic, or basic?

18.25 (a) What is the pH of 5.04×10^{-3} M HI? Is the solution neutral, acidic, or basic?

(b) What is the pOH of $2.55 M \text{ Ba}(\text{OH})_2$? Is the solution neutral, acidic, or basic?

18.26 (a) What is the pH of 7.52×10⁻⁴ M CsOH? Is the solution neutral, acidic, or basic?

(b) What is the pOH of 1.59×10^{-3} M HClO₄? Is the solution neutral, acidic, or basic?

18.27 (a) What are [H₃O⁺], [OH⁻], and pOH in a solution with a pH of 9.78?

(b) What are [H₃O⁺], [OH⁻], and pH in a solution with a pOH of 10.43?

18.28 (a) What are $[H_3O^+]$, $[OH^-]$, and pOH in a solution with a pH of 3.47?

(b) What are [H₃O⁺], [OH⁻], and pH in a solution with a pOH of 4.33?

18.29 (a) What are [H₃O⁺], [OH⁻], and pOH in a solution with a pH of 2.77?

(b) What are [H₃O⁺], [OH⁻], and pH in a solution with a pOH of 5.18?

18.30 (a) What are [H₃O⁺], [OH⁻], and pOH in a solution with a pH of 8.97?

(b) What are $[H_3O^+]$, $[OH^-]$, and pH in a solution with a pOH of 11.27?

18.31 How many moles of H₃O⁺ or OH⁻ must you add per liter of HA solution to adjust its pH from 3.25 to 3.65? Assume a negligible volume change.

18.32 How many moles of H₃O⁺ or OH[−] must you add per liter of HA solution to adjust its pH from 9.33 to 9.07? Assume a negligible volume change.

18.33 How many moles of H₃O⁺ or OH⁻ must you add to 6.5 L of HA solution to adjust its pH from 4.82 to 5.22? Assume a negligible volume change.

18.34 How many moles of H₃O⁺ or OH⁻ must you add to 87.5 mL of HA solution to adjust its pH from 8.92 to 6.33? Assume a negligible volume change.

Problems in Context

18.35 Although the text asserts that water is an extremely weak electrolyte, parents commonly warn their children of the danger of swimming in a pool or lake during a lightning storm. Explain.

18.36 Like any equilibrium constant, K_w changes with temperature.

(a) Given that autoionization is an endothermic process, does $K_{\rm w}$ increase or decrease with rising temperature? Explain with a reaction that includes heat as reactant or product.

(b) In many medical applications, the value of $K_{\rm w}$ at 37°C (body temperature) may be more appropriate than the value at 25°C, 1.0×10^{-14} . The pH of pure water at 37°C is 6.80. Calculate $K_{\rm w}$, pOH, and [OH⁻] at this temperature.

Proton Transfer and the Brønsted-Lowry Acid-Base Definition

(Sample Problems 18.4 and 18.5)

Concept Review Questions

18.37 How do the Arrhenius and Brønsted-Lowry definitions of an acid and a base differ? How are they similar? Name two Brønsted-Lowry bases that are not considered Arrhenius bases. Can you do the same for acids? Explain.

18.38 What is a conjugate acid-base pair? What is the relationship between the two members of the pair?

- 18.39 A Brønsted-Lowry acid-base reaction proceeds in the net direction in which a stronger acid and stronger base form a weaker acid and weaker base. Explain.
- 18.40 What is an amphoteric species? Name one and write balanced equations that show why it is amphoteric.

Skill-Building Exercises (grouped in similar pairs)

- 18.41 Write balanced equations and K_n expressions for these Brønsted-Lowry acids in water:
 - (b) C₆H₅COOH (c) HSO₄ (a) H₃PO₄
- 18.42 Write balanced equations and Ka expressions for these Brønsted-Lowry acids in water:
 - (a) HCOOH (b) HClO₃
- (c) H2AsO4
- 18.43 Give the formula of the conjugate base:
- (a) HCl
- (b) H₂CO₃
- (c) H₂O
- 18.44 Give the formula of the conjugate base:
 - (a) HPO₄²⁻ (b) NH4+
- (c) HS
- 18.45 Give the formula of the conjugate acid:
- (a) NH₃ (b) NH2
- (c) nicotine, C10H14N2
- 18.46 Give the formula of the conjugate acid:
- (a) O2 (b) SO₄2
- (c) H₂O
- 18.47 In each equation, label the acids, bases, and conjugate acidbase pairs:
 - (a) $HCl + H_2O \implies Cl^- + H_3O^+$

 - (b) $\text{HClO}_4 + \text{H}_2 \text{SO}_4 \Longrightarrow \text{ClO}_4^- + \text{H}_3 \text{SO}_4^+$ (c) $\text{HPO}_4^{2-} + \text{H}_2 \text{SO}_4 \Longrightarrow \text{H}_2 \text{PO}_4^- + \text{HSO}_4^-$
- 18.48 In each equation, label the acids, bases, and conjugate acidbase pairs:
- (a) $NH_3 + HNO_3 \implies NH_4^+ + NO_3^-$
- (b) $O^{2-} + H_2O \implies OH^- + OH^-$
- (c) $NH_4^+ + BrO_3^- \Longrightarrow NH_3 + HBrO_3$
- 18.49 In each equation, label the acids, bases, and conjugate acidbase pairs:
- (a) $NH_3 + H_3PO_4 \implies NH_4^+ + H_2PO_4^-$
- (b) $CH_3O^- + NH_3 \Longrightarrow CH_3OH + NH_2^-$ (c) $HPO_4^{2-} + HSO_4^- \Longrightarrow H_2PO_4^- + SO_4^{2-}$
- 18.50 In each equation, label the acids, bases, and conjugate acidbase pairs:
- (a) $NH_4^+ + CN^- \implies NH_3 + HCN$
- (b) $H_2O + HS^- \Longrightarrow OH^- + H_2S$
- (c) $HSO_3^- + CH_3NH_2 \Longrightarrow SO_3^{2-} + CH_3NH_3^+$
- 18.51 Write balanced net ionic equations for the following reactions, and label the conjugate acid-base pairs:
- (a) $NaOH(aq) + NaH_2PO_4(aq) \Longrightarrow H_2O(l) + Na_2HPO_4(aq)$
- (b) KHSO₄ $(aq) + K_2CO_3(aq) \Longrightarrow K_2SO_4(aq) + KHCO_3(aq)$
- 18.52 Write balanced net ionic equations for the following reactions, and label the conjugate acid-base pairs:
- (a) $HNO_3(aq) + Li_2CO_3(aq) \Longrightarrow LiNO_3(aq) + LiHCO_3(aq)$
- (b) $2NH_4Cl(aq) + Ba(OH)_2(aq) \Longrightarrow$
 - $2H_2O(l) + BaCl_2(aq) + 2NH_3(aq)$
- 18.53 The following aqueous species constitute two conjugate acid-base pairs. Use them to write one acid-base reaction with $K_c > 1$ and another with $K_c < 1$; HS⁻, Cl⁻, HCl, H₂S.
- 18.54 The following aqueous species constitute two conjugate acid-base pairs. Use them to write one acid-base reaction with $K_c > 1$ and another with $K_c < 1$: NO_3^- , F^- , HF, HNO₃.

- 18.55 Use Figure 18.9 (p. 781) to determine whether $K_c > 1$ for
- (a) HCl + NH₃ == NH₄⁺ + Cl⁻
- (b) $H_2SO_3 + NH_3 \Longrightarrow HSO_3^- + NH_4^+$
- **18.56** Use Figure 18.9 (p. 781) to determine whether $K_c > 1$ for
- (a) $OH^- + HS^- \Longrightarrow H_2O + S^{2-}$ (b) $HCN + HCO_3^- \Longrightarrow H_2CO_3 + CN^-$
- 18.57 Use Figure 18.9 (p. 781) to determine whether $K_c < 1$ for
- (a) $NH_4^+ + HPO_4^{2-} \Longrightarrow NH_3 + H_2PO_4^{-}$ (b) $HSO_3^- + HS^- \Longrightarrow H_2SO_3 + S^{2-}$
- **18.58** Use Figure 18.9 (p. 781) to determine whether $K_c < 1$ for
- (a) $H_2PO_4^- + F^- \implies HPO_4^{2-} + HF$
- (b) $CH_3COO^- + HSO_4^- \Longrightarrow CH_3COOH + SO_4^{2-}$

Solving Problems Involving Weak-Acid Equilibria

(Sample Problems 18.6 to 18.8)

Concept Review Questions

- 18.59 In each of the following cases, would you expect the concentration of acid before and after dissociation to be nearly the same or very different? Explain your reasoning.
 - (a) A concentrated solution of a strong acid
 - (b) A concentrated solution of a weak acid
 - (c) A dilute solution of a weak acid
 - (d) A dilute solution of a strong acid
- 18.60 A sample of 0.0001 M HCl has [H₃O⁺] close to that of a sample of 0.1 M CH3COOH. Are acetic acid and hydrochloric acid equally strong in these samples? Explain.
- 18.61 In which of the following solutions will [H₃O⁺] be approximately equal to [CH3COO]: (a) 0.1 M CH3COOH; (b) 1×10⁻⁷ M CH₃COOH; (c) a solution containing both 0.1 M CH₃COOH and 0.1 M CH₃COONa? Explain.
- **18.62** Why do successive K_a 's decrease for all polyprotic acids?

Skill-Building Exercises (grouped in similar pairs)

- 18.63 A 0.15 M solution of butanoic acid, CH₃CH₂CH₂COOH, contains $1.51 \times 10^{-3} M H_3 O^+$. What is the K_a of butanoic acid?
- 18.64 A 0.035 M solution of a weak acid (HA) has a pH of 4.88. What is the K_a of the acid?
- 18.65 Nitrous acid, HNO₂, has a K_a of 7.1×10^{-4} . What are [H₃O⁺], [NO₂⁻], and [OH⁻] in 0.50 M HNO₂?
- 18.66 Hydrofluoric acid, HF, has a K_a of 6.8×10⁻⁴. What are $[H_3O^+]$, $[F^-]$, and $[OH^-]$ in 0.75 M HF?
- 18.67 Chloroacetic acid, ClCH2COOH, has a pK2 of 2.87. What are [H₃O⁺], pH, [ClCH₂COO⁻], and [ClCH₂COOH] in 1.05 M
- CICH2COOH?
- 18.68 Hypochlorous acid, HClO, has a pK, of 7.54. What are $[H_3O^+]$, pH, $[ClO^-]$, and [HClO] in 0.115 M HClO?
- 18.69 In a 0.25 M solution, a weak acid is 3.0% dissociated.
- (a) Calculate the [H₃O⁺], pH, [OH⁻], and pOH of the solution.
- (b) Calculate K_a of the acid.
- 18.70 In a 0.735 M solution, a weak acid is 12.5% dissociated.
 - (a) Calculate the [H₃O⁺], pH, [OH⁻], and pOH of the solution.
 - (b) Calculate K_a of the acid.
- 18.71 A 0.250-mol sample of HX is dissolved in enough H2O to form 655 mL of solution. If the pH of the solution is 3.44, what is the Ka of HX?
- 18.72 A 4.85×10^{-3} -mol sample of HY is dissolved in enough H₂O to form 0.095 L of solution. If the pH of the solution is 2.68, what is the K_a of HY?

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- 18.73 The weak acid HZ has a K_a of 1.55×10^{-4} .
- (a) Calculate the pH of 0.075 M HZ.
- (b) Calculate the pOH of 0.045 M HZ.
- 18.74 The weak acid HQ has a pK, of 4.89.
- (a) Calculate the $[H_3O^+]$ of $3.5 \times 10^{-2} M$ HQ.
- (b) Calculate the [OH] of 0.65 M HQ.
- **18.75** (a) Calculate the pH of 0.175 M HY, if $K_a = 1.00 \times 10^{-4}$.
- (b) Calculate the pOH of 0.175 M HX, if $K_a = 1.00 \times 10^{-2}$.
- **18.76** (a) Calculate the pH of 0.553 M KHCO₃; K_a of HCO₃⁻ = 4.7×10^{-11} .
- (b) Calculate the pOH of 0.044 M HIO₃; K_a of HIO₃ = 0.16.
- 18.77 Use Appendix C to calculate the percent dissociation of 0.25 M benzoic acid, C₆H₅COOH.
- **18.78** Use Appendix C to calculate the percent dissociation of 0.050 M CH₃COOH.
- 18.79 Use Appendix C to calculate [H₂S], [HS⁻], [S²⁻], [H₃O⁺], pH, [OH⁻], and pOH in a 0.10 M solution of the diprotic acid hydrosulfuric acid.
- **18.80** Use Appendix C to calculate [H₂C₂O₄], [HC₂O₄], [C₂O₄], [H₃O⁺], pH, [OH⁻], and pOH in a 0,200 M solution of the diprotic acid oxalic acid.

Problems in Context

- **18.81** Acetylsalicylic acid (aspirin), $HC_9H_7O_4$, is the most widely used pain reliever and fever reducer. Find the pH of 0.018 M aqueous aspirin at body temperature (K_a at $37^{\circ}C = 3.6 \times 10^{-4}$).
- 18.82 Formic acid, HCOOH, the simplest carboxylic acid, has many uses in the textile and rubber industries. It is an extremely caustic liquid that is secreted as a defense by many species of ants (family Formicidae). Calculate the percent dissociation of 0.50 M HCOOH.

Weak Bases and Their Relation to Weak Acids

(Sample Problems 18.9 and 18.10)

Concept Review Questions

- 18.83 What is the key structural feature of all Brønsted-Lowry bases? How does this feature function in an acid-base reaction?
- 18.84 Why are most anions basic in H₂O? Give formulas of four anions that are not basic.
- **18.85** Except for the Na⁺ spectator ion, aqueous solutions of CH₃COOH and CH₃COONa contain the same species. (a) What are the species (other than H₂O)? (b) Why is 0.1 M CH₃COOH acidic and 0.1 M CH₃COONa basic?

Skill-Building Exercises (grouped in similar pairs)

- 18.86 Write balanced equations and K_b expressions for these Brønsted-Lowry bases in water:
 - (a) Pyridine, C₅H₅N (b) CO₃²⁻
- **18.87** Write balanced equations and K_b expressions for these Brønsted-Lowry bases in water:
- (a) Beozoate ion, C₆H₅COO (b) (CH₃)₃N
- 18.88 Write balanced equations and K_b expressions for these Brønsted-Lowry bases in water:
- (a) Hydroxylamine, HO-NH₂ (b) HPO₄²⁻
- **18.89** Write balanced equations and K_b expressions for these Brønsted-Lowry bases in water:
- (a) Guanidine, $(H_2N)_2C = NH$ (double-bonded N is most basic)
- (b) Acetylide ion, HC≡C

- 18.90 What is the pH of 0.050 M dimethylamine?
- 18.91 What is the pH of 0.12 M diethylamine?
- 18.92 What is the pH of 0.15 M ethanolamine?
- 18.93 What is the pH of 0.26 M aniline?
- 18.94 (a) What is the K_b of the acetate ion?
- (b) What is the K_a of the anilinium ion, $C_6H_5NH_3^{+}$?
- **18.95** (a) What is the K_b of the benzoate ion, $C_6H_5COO^-$?
 - (b) What is the K_n of the 2-hydroxyethylammonium ion, $HOCH_2CH_2NH_3^+$ (p K_h of $HOCH_2CH_2NH_2 = 4.49$)?
- 18.96 (a) What is the pK_b of ClO_2^- ?
- (b) What is the pK_a of the dimethylammonium ion, $(CH_3)_2NH_2^+$?
- **18.97** (a) What is the p K_b of NO₂⁻?
 - (b) What is the pKa of the hydrazinium ion, H2N-NH3+
 - $(K_b \text{ of hydrazine} = 8.5 \times 10^{-7})$?
- 18.98 (a) What is the pH of 0.050 M KCN?
- (b) What is the pH of 0.30 M triethylammonium chloride, (CH₃CH₂)₃NHCl?
- **18.99** (a) What is the pH of 0.100 M sodium phenolate, C₆H₅ONa, the sodium salt of phenol?
- (b) What is the pH of 0.15 M methylammonium bromide, CH₃NH₃Br (K_b of CH₃NH₂ = 4.4×10⁻⁴)?
- 18.100 (a) What is the pH of 0.53 M potassium formate, HCOOK?
- (b) What is the pH of 1.22 M NH₄Br?
- **18.101** (a) What is the pH of 0.75 M NaF? (b) What is the pH of 0.88 M pyridinium chloride, C₅H₅NHCl?

Problems in Context

- 18.102 Sodium hypochlorite solution, sold as "chlorine bleach," is recognized as a potentially dangerous household product. The dangers arise from its basicity and from ClO⁻, the active bleaching ingredient. What is [OH⁻] in an aqueous solution that is 5.0% NaClO by mass? What is the pH of the solution? (Assume d of solution = 1.0 g/mL.)
- **18.103** Codeine ($C_{18}H_{21}NO_3$) is a narcotic pain reliever that forms a salt with HCl. What is the pH of 0.050 M codeine hydrochloride (pK_b of codeine = 5.80)?

Molecular Properties and Acid Strength

Concept Review Questions

- 18.104 Across a period, how does the electronegativity of a non-metal affect the acidity of its binary hydride?
- 18.105 How does the atomic size of a nonmetal affect the acidity of its binary hydride?
- 18.106 A strong acid has a weak bond to its acidic proton, whereas a weak acid has a strong bond to its acidic proton. Explain.
- 18.107 Perchloric acid, HClO₄, is the strongest of the halogen oxoacids, and hypoiodous acid, HIO, is the weakest. What two factors govern this difference in acid strength?

Skill-Building Exercises (grouped in similar pairs)

- 18.108 Choose the stronger acid in each of the following pairs:
- (a) H_2SeO_3 or H_2SeO_4 (b) H_3PO_4 or H_3AsO_4 (c) H_2S or H_2Te
- **18.109** Choose the *weaker* acid in each of the following pairs:
- (a) HBr or H₂Se (b) HClO₄ or H₂SO₄ (c) H₂SO₃ or H₂SO₄
- 18.110 Choose the stronger acid in each of the following pairs:
- (a) H₂Se or H₃As (b) B(OH)₃ or Al(OH)₃ (c) HBrO₂ or HBrO
- **18.111** Choose the *weaker* acid in each of the following pairs:
- (a) HI or HBr (b) H₃AsO₄ or H₂SeO₄ (c) HNO₃ or HNO₂

18.112 Use Appendix C to choose the solution with the *lower* pH:

(a) 0.1 M CuSO₄ or 0.05 M Al₂(SO₄)₃

(b) 0.1 M ZnCl2 or 0.1 M PbCl2

18.113 Use Appendix C to choose the solution with the lower pH:

(a) 0.1 M FeCl₃ or 0.1 M AlCl₃

(b) 0.1 M BeCl₂ or 0.1 M CaCl₂

18.114 Use Appendix C to choose the solution with the higher pH:

(a) 0.1 M Ni(NO₃)₂ or 0.1 M Co(NO₃)₂ (b) 0.1 M Al(NO₃)₃ or 0.1 M Cr(NO₃)₃

18.115 Use Appendix C to choose the solution with the higher pH:

(a) 0.1 M NiCl₂ or 0.1 M NaCl

(b) 0.1 M Sn(NO₃)₂ or 0.1 M Co(NO₃)₂

Acid-Base Properties of Salt Solutions

(Sample Problems 18.11 and 18.12)

Concept Review Questions

18.116 What determines whether an aqueous solution of a salt will be acidic, basic, or neutral? Give an example of each type of salt.18.117 Why is aqueous NaF basic but aqueous NaCl neutral?

18.118 The NH₄⁺ ion forms acidic solutions, and the C₂H₃O₂⁻ ion forms basic solutions. However, a solution of ammonium acetate is almost neutral. Do all of the ammonium salts of weak acids form neutral solutions? Explain your answer.

Skill-Building Exercises (grouped in similar pairs)

18.119 Explain with equations and calculations, when necessary, whether an aqueous solution of each of these salts is acidic, basic, or neutral: (a) KBr; (b)NH₄I; (c) KCN.

18.120 Explain with equations and calculations, when necessary, whether an aqueous solution of each of these salts is acidic, basic, or neutral: (a) Cr(NO₃)₃; (b) NaHS; (c) Zn(CH₃COO)₂.

18.121 Explain with equations and calculations, when necessary, whether an aqueous solution of each of these salts is acidic, basic, or neutral: (a) Na₂CO₃; (b) CaCl₂; (c) Cu(NO₃)₂.

18.122 Explain with equations and calculations, when necessary, whether an aqueous solution of each of these salts is acidic, basic, or neutral: (a) CH₃NH₃Cl; (b) KClO₄; (c) CoF₂.

18.123 Explain with equations and calculations, when necessary, whether an aqueous solution of each of these salts is acidic, basic, or neutral: (a) SrBr₂; (b) Ba(CH₃COO)₂; (c) (CH₃)₂NH₂Br.

18.124 Explain with equations and calculations, when necessary, whether an aqueous solution of each of these salts is acidic, basic, or neutral: (a) Fe(HCOO)₃; (b) KHCO₃; (c) K₂S.

18.125 Explain with equations and calculations, when necessary, whether an aqueous solution of each of these salts is acidic, basic, or neutral: (a) (NH₄)₃PO₄; (b) Na₂SO₄; (c) LiClO.

18.126 Explain with equations and calculations, when necessary, whether an aqueous solution of each of these salts is acidic, basic, or neutral: (a) Pb(CH₃COO)₂; (b) Cr(NO₂)₃; (c) CsI.

18.127 Rank the following salts in order of increasing pH of their 0.1 M aqueous solutions:

(a) KNO₃, K₂SO₃, K₂S, Fe(NO₃)₂

(b) NH₄NO₃, NaHSO₄, NaHCO₃, Na₂CO₃

18.128 Rank the following salts in order of *decreasing* pH of their 0.1 M aqueous solutions:

(a) FeCl2, FeCl3, MgCl2, KClO2

(b) NH4Br, NaBrO2, NaBr, NaClO2

Generalizing the Brønsted-Lowry Concept: The Leveling Effect

Concept Review Questions

18.129 The methoxide ion, CH₃O⁻, and amide ion, NH₂⁻, are very strong bases that are "leveled" by water. What does this mean? Write the reactions that occur in the leveling process. What species do the two leveled solutions have in common?

18.130 Explain the differing extents of dissociation of H₂SO₄ in CH₃COOH, H₂O, and NH₃.

18.131 In H₂O, HF is weak and the other hydrohalic acids are equally strong. In NH₃, however, all the hydrohalic acids are equally strong. Explain.

Electron-Pair Donation and the Lewis Acid-Base Definition (Sample Problem 18.13)

Concept Review Questions

18.132 What feature must a molecule or ion have for it to act as a Lewis base? A Lewis acid? Explain the roles of these features.

18.133 How do Lewis acids differ from Brønsted-Lowry acids? How are they similar? Do Lewis bases differ from Brønsted-Lowry bases? Explain.

18.134 (a) Is a weak Brønsted-Lowry base necessarily a weak Lewis base? Explain with an example.

(b) Identify the Lewis bases in the following reaction:

$$Cu(H_2O)_4^{2+}(aq) + 4CN^{-}(aq) \Longrightarrow$$

 $Cu(CN)_4^{2-}(aq) + 4H_2O(l)$

(c) Given that $K_c > 1$ for the reaction in part (b), which Lewis base is stronger?

18.135 In which of the three concepts of acid-base behavior discussed in the text can water be a product of an acid-base reaction? In which is it the only product?

18.136 (a) Give an example of a substance that is a base in two of the three acid-base definitions, but not in the third.

(b) Give an example of a *substance* that is an acid in one of the three acid-base definitions, but not in the other two.

Skill-Building Exercises (grouped in similar pairs)

18.137 Which are Lewis acids and which are Lewis bases?

(a) Cu²⁺ (b) Cl⁻ (c) SnCl₂ (d) OF₂

18.138 Which are Lewis acids and which are Lewis bases?

(a) Na⁺ (b) NH₃ (c) CN⁻ (d) BF₃

18.139 Which are Lewis acids and which are Lewis bases?
 (a) BF₃
 (b) S²⁺
 (c) SO₃²⁻
 (d) SO₃

18.140 Which are Lewis acids and which are Lewis bases?

(a) Mg²⁺ (b) OH⁻ (c) SiF₄ (d) BeCl₂

18.141 Identify the Lewis acid and Lewis base in each equation:

(a) $Na^+ + 6H_2O \implies Na(H_2O)_6$

(b) $CO_2 + H_2O \Longrightarrow H_2CO_3$

(c) $F^- + BF_3 \Longrightarrow BF_4^-$

18.142 Identify the Lewis acid and Lewis base in each equation:

(a) $Fe^{3+} + 2H_2O \implies FeOH^{2+} + H_3O^+$

(b) $H_2O + H^- \implies OH^- + H_2$

(c) 4CO + Ni = Ni(CO)4

18.143 Classify the following as Arrhenius, Brønsted-Lowry, or Lewis acid-base reactions. A reaction may fit all, two, one, or none of the categories:

(a) $Ag^+ + 2NH_3 \implies Ag(NH_3)_2^+$

(b) $H_2SO_4 + NH_3 \implies HSO_4^- + NH_4^+$

Problems

811

(c) $2HCl \rightleftharpoons H_2 + Cl_2$ (d) AlCl₃ + Cl - AlCl₄

18.144 Classify the following as Arrhenius, Brønsted-Lowry, or Lewis acid-base reactions. A reaction may fit all, two, one, or none of the categories:

(a) $Cn^{2+} + 4Cl^{-} \implies CuCl_4^{2-}$

(b) $AI(OH)_3 + 3HNO_3 \implies AI^{3+} + 3H_2O + 3NO_3^-$

(c) $N_2 + 3H_2 \implies 2NH_3$

(d) CN + H₂O ⇒ HCN + OH

Comprehensive Problems

18.145 Pantothenic acid (C₉H₁₇NO₅; vitamin B₃) is shown below. This biologically active molecule is an optical isomer that behaves like a monoprotic Brønsted-Lowry acid in water.



(a) Use the molecular formula to write the equation for the reaction of pantothenic acid with water and the K_a expression.

(b) Which C atom is the chiral center?

18.146 The pK_a of acetic acid is 4.76 in pure water and 4.53 in seawater. In which solvent is it a stronger acid?

18.147 Bodily processes in humans maintain the pH of blood within a narrow range. In fact, a condition called acidosis occurs if the blood pH goes below 7.35, and another called alkalosis occurs if the pH goes above 7.45. Given that the pK_w of blood is 13.63 at 37°C (body temperature), what is the normal range of [H₃O⁺] and of [OH⁻] in blood?

18.148 One use of phenol, C₆H₅OH, is as a disinfectant. In water its pK_a is 10.0, but in methanol it is 14.4. (a) Why are the values different? (b) Use these two values to decide whether methanol is a stronger or weaker base than water. (c) Write the dissociation reaction of phenol in methanol. (d) Write an expression for the autoionization constant of methanol.

18.149 When carbon dioxide dissolves in water, it undergoes a multistep equilibrium process, with $K_{\text{overall}} = 4.5 \times 10^{-7}$, which is simplified to the following:

$$CO_2(g) + H_2O(l) \Longrightarrow H_2CO_3(aq)$$

 $H_2CO_3(aq) + H_2O(l) \implies HCO_3^-(aq) + H_3O^+(aq)$

(a) Classify each step as a Lewis or a Brønsted-Lowry reaction. (b) What is the pH of nonpolluted rainwater in equilibrium with clean air (P_{CO_2} in clean air = 3.2×10^{-4} atm; Henry's law con-

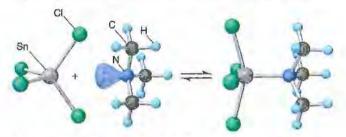
stant for CO_2 at 25°C is 0.033 mol/L*atm)? (c) What is $[CO_3^{2-}]$ in rainwater (K_a of $HCO_3^{-} = 4.7 \times 10^{-11}$)?

(d) If the partial pressure of CO₂ in clean air doubles in the next few decades, what will the pH of rainwater become?

18.150 Seashells are mostly calcium carbonate, which reacts with H₃O⁺ according to the equation

$$CaCO_3(s) + H_3O^+(aq) \Longrightarrow Ca^{2+}(aq) + HCO_3^-(aq) + H_2O(l)$$

If K_w increases at higher pressure, will seashells dissolve more rapidly near the surface of the ocean or at great depths? Explain. 18.151 Many molecules with central atoms from Period 3 or higher take part in Lewis acid-base reactions in which the central atom expands its valence shell. SnCl4 reacts with (CH3)3N as follows:



(a) Identify the Lewis acid and the Lewis base in the reaction.

(b) Give the nl designation of the sublevel of the central atom in the acid that accepts the lone pair.

18.152 A chemist makes four successive 1:10 dilutions of 1.0×10^{-5} M HCl. Calculate the pH of the original solution and of each diluted solution (through $1.0 \times 10^{-9} M$ HCl).

18.153 At 25°C, the p K_w of seawater is 13.22; this value is lower than that for water as a result of the dissolved salts. If the pH of a sample of seawater is 7.54, what is the pOH of the sample?

18.154 Chlorobenzene, C₆H₅Cl, is a key intermediate in the manufacture of many aromatic compounds, including aniline dyes and chlorinated pesticides. It is made by the FeCl3-catalyzed chlorination of benzene in this series of steps:

(1) Cl₂ + FeCl₃ ⇒ FeCl₅ (or Cl⁺FeCl₄⁻)

(2) $C_6H_6 + Cl^+FeCl_4^- \rightleftharpoons C_6H_6Cl^+ + FeCl_4^-$ (3) $C_6H_6Cl^+ \rightleftharpoons C_6H_5Cl + H^+$

(4) H⁺ + FeCl₄ = HCl + FeCl₃

(a) Which of the step(s) is (are) Lewis acid-base reactions?

(b) Identify the Lewis acids and bases in each of those steps.

18.155 Hydrogen peroxide, H_2O_2 (p $K_a = 11.75$), is commonly used as a bleaching agent and an antiseptic. The product sold in stores is 3% H₂O₂ by mass and contains 0.001% phosphoric acid by mass to stabilize the solution. Which contributes more H₃O⁺ to this commercial solution, the H₂O₂ or the H₃PO₄?

18.156 The strengths of acids and bases are directly related to their strengths as electrolytes (Section 4.4).

(a) Is the electrical conductivity of 0.1 M HCl higher, lower, or the same as that of 0.1 M CH₃COOH? Explain.

(b) Is the electrical conductivity of 1×10^{-7} M HCl higher, lower, or the same as that of 1×10^{-7} M CH₃COOH? Explain.

18.157 Esters, RCOOR', are formed by the reaction of carboxylic acids, RCOOH, and alcohols, R'OH, where R and R' are hydrocarbon groups. Many esters are responsible for the odors of fruit and, thus, have important uses in the food and cosmetics industries. The first two steps in the mechanism of ester formation are

Identify the Lewis acids and Lewis bases in these two steps.

18.158 Three beakers contain 100. mL of 0.10 M acid, either HCl, HClO₂, or HClO. (a) Find the pH of each. (b) Describe quantitatively how to make the pH equal in the beakers through the addition of water only.

18.159 Human urine has a normal pH of 6.2. If a person eliminates an average of 1250. mL of urine per day, how many H+ ions are eliminated per week?

18.160 Liquid ammonia autoionizes like water:

 $2NH_3(l) \longrightarrow NH_4^+(am) + NH_2^-(am)$

where (am) represents solvation by ammonia.

(a) Write the ion-product constant expression, Kam.

(b) What are the strongest acid and strongest base that can exist in liquid ammonia?

(c) HNO3 and HCOOH are leveled in liquid NH3. Explain with equations.

(d) At the boiling point (-33°C), $K_{am} = 5.1 \times 10^{-27}$. Calculate [NH₄⁺] at this temperature.

(e) Pure sulfuric acid also autoionizes. Write the ion-product constant expression, K_{sulf}, and find the concentration of the conjugate base at 20°C ($K_{\text{sulf}} = 2.7 \times 10^{-4}$ at 20°C).

18.161 Autoionization (see Problem 18.160) occurs in methanol (CH₃OH) and in ethylenediamine (NH₂CH₂CH₂NH₂).

(a) The autoionization constant of methanol (K_{met}) is 2×10^{-17} . What is [CH3O] in pure CH3OH?

(b) The concentration of NH2CH2CH2NH3+ in pure NH2CH2CH2NH2 is 2×10-8 M. What is the autoionization constant of ethylenediamine (K_{en}) ?

18.162 Thiamine hydrochloride (C₁₂H₁₈ON₄SCl₂) is a watersoluble form of thiamine (vitamin B₁; $K_a = 3.37 \times 10^{-7}$). How many grams of the hydrochloride must be dissolved in 10.00 mL of water to give a pH of 3.50?

18.163 Tris(hydroxymethyl)aminomethane, known as TRIS or THAM, is a water-soluble base that is a reactant in the synthesis of surfactants and pharmaceuticals, an emulsifying agent in cosmetic creams and lotions, and a component of various cleaning and polishing mixtures for textiles and leather. In biomedical research, solutions of TRIS are used to maintain nearly constant pH for the study of enzymes and other cellular components. Given that the p K_b is 5.91, calculate the pH of 0.060 M TRIS.

18.164 When Fe³⁺ salts are dissolved in water, the solution becomes acidic due to formation of Fe(H₂O)₅OH²⁺ and H₃O⁺. The overall process involves both Lewis and Brønsted-Lowry acid-base reactions. Write the equations for the process.

18.165 Vinegar is a 5.0% (w/v) solution of acetic acid in water. What is the pH of vinegar?

18.166 How would you differentiate between a strong and a weak monoprotic acid from the results of the following procedures?

(a) Electrical conductivity of an equimolar solution of each acid is measured.

(b) Equal molarities of each are tested with pH paper.

(e) Zinc metal is added to solutions of equal concentration.

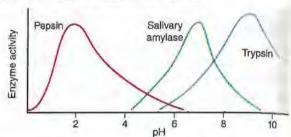
18.167 At 50°C and 1 atm, $K_w = 5.19 \times 10^{-14}$. Calculate parts (a)-(c) under these conditions:

(a) [H₃O⁺] in pure water (b) [H₃O⁺] in 0.010 *M* NaOH (c) [OH⁻] in 0.0010 *M* HClO₄

(d) Calculate [H₃O⁺] in 0.0100 M KOH at 100°C and 1000 atm pressure $(K_w = 1.10 \times 10^{-12})$.

(e) Calculate the pH of pure water at 100°C and 1000 atm.

18.168 The catalytic efficiency of an enzyme is called its activity and refers to the rate at which it catalyzes the reaction. Most enzymes have optimum activity over a relatively narrow pH range. which is related to the pH of the local cellular fluid. The pH profiles of three digestive enzymes are shown.



Salivary amylase begins digestion of starches in the mouth and has optimum activity at a pH of 6.8; pepsin begins protein digestion in the stomach and has optimum activity at a pH of 2.0: and trypsin, released in pancreatic juices, continues protein digestion in the small intestine and has optimum activity at a pH of Calculate [H₃O⁺] in the local cellular fluid for each enzyme.

18.169 Acetic acid has a K_a of 1.8×10^{-5} , and ammonia has a K_b of 1.8×10⁻⁵. Find [H₃O⁺], [OH⁻], pH, and pOH for (a) 0.240 M acetic acid and (b) 0.240 M ammonia.

18.170 Sodium phosphate has industrial uses ranging from clarifying crude sugar to manufacturing paper. Sold as TSP, it is used in solution to remove boiler scale and to wash painted brick and coucrete. What is the pH of a solution containing 33 g of Na₃PO₄ per liter? What is [OH] of this solution?

18.171 The Group 5A(15) hydrides react with boron trihalides in a reversible Lewis acid-base reaction. When 0.15 mol of PH3BCl3(s) is introduced into a 3.0-L container at a certain temperature, 8.4×10^{-3} mol of PH₃ is present at equilibrium: $PH_3BCl_3(s) \Longrightarrow PH_3(g) + BCl_3(g)$.

(a) Calculate K_c for the reaction at this temperature.

(b) Draw a Lewis structure for the reactant.

18.172 A 1.000 m solution of chloroacetic acid (CICH₂COOH) freezes at -1.93°C. Use these data to find the K_a of chloroacetic acid. (Assume the molarities equal the molalities.)

18.173 Sodium stearate (C₁₇H₃₅COONa) is a major component of bar soap (see Chapter 13, p. 498). The Ka of the stearic acid is 1.3×10⁻⁵. What is the pH of 10.0 mL of a solution containing 0.42 g of sodium stearate?

18.174 Calcium propionate [Ca(CH3CH2COO)2; calcium propanoate] is a mold inhibitor used in food, tobacco, and pharmaceuticals. (a) Use balanced equations to show whether aqueous calcium propionate is acidic, basic, or neutral. (b) Use Appendix C to find the pH of a solution made by dissolving 7.05 g of Ca(CH₃CH₂COO)₂ in water to give 0.500 L of solution.

18.175 Carbon dioxide is less soluble in dilute HCl than in dilute NaOH. Explain.

18.176 (a) If $K_{\rm w} = 1.139 \times 10^{-15}$ at 0°C and 5.474×10⁻¹⁴ at 50°C, find [H₃O⁺] and pH of water at 0°C and 50°C.

(b) The autoionization constant for heavy water (deuterium oxide, D_2O) is 3.64×10^{-16} at $0^{\circ}C$ and 7.89×10^{-15} at $50^{\circ}C$. Find [D₃O⁺] and pD of heavy water at 0°C and 50°C.

(c) Suggest a reason for these differences.

18.177 HX (M = 150. g/mol) and HY (M = 50.0 g/mol) are weak acids. A solution of 12.0 g/L of HX has the same pH as one containing 6.00 g/L of HY. Which is the stronger acid? Why?

18.178 In his acid-base studies, Arrhenius discovered an important fact involving reactions like the following:

$$KOH(aq) + HNO_3(aq) \longrightarrow ?$$

 $NaOH(aq) + HCl(aq) \longrightarrow ?$

(a) Complete the reactions and use the data for the individual ions in Appendix B to calculate each ΔH_{rxn}^0 .

(b) Explain your results and use them to predict ΔH_{rxn}^0 for

$$KOH(aq) + HCl(aq) \longrightarrow ?$$

18.179 Amines have foul odors, Putrescine [NH2(CH2)4NH2], once thought to be found only in rotting animal tissue, is now known to be a component of all cells and essential for normal and abnormal (cancerous) growth. It also plays a key role in formation of GABA, a neurotransmitter. A 0.10 M aqueous solution of putrescine has $[OH^-] = 2.1 \times 10^{-3}$. What is the K_b ?

18.180 Nitrogen is discharged from wastewater treatment facilities into rivers and streams, usually as NH3 and NH4+:

 $NH_3(aq) + H_2O(l) \implies NH_4^+(aq) + OH^-(aq)$ $K_b = 1.76 \times 10^{-5}$ One strategy for removing it is to raise the pH and "strip" the NH₃ from solution by bubbling air through the water. (a) At pH 7.00, what fraction of the total nitrogen in solution is NH₃, defined as [NH₃]/([NH₃] + [NH₄⁺])? (b) What is the fraction at pH 10.00? (c) Explain the basis of ammonia stripping.

18.181 Polymers and other large molecules are not very soluble in water, but their solubility increases if they have charged groups. (a) Casein is a protein in milk that contains many carboxylic acid groups on its side chains. Explain how the solubility of casein in water varies with pH.

(b) Histones are proteins that are essential to the proper function of DNA. They are weakly basic due to the presence of side chains with -NH2 and =NH groups. Explain how the solubility of histones in water varies with pH.

18.182 Hemoglobin (Hb) transports oxygen in the blood:

$$HbH^+(aq) + O_2(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + HbO_2(aq)$$

In blood, $[H_3O^+]$ is held nearly constant at 4×10^{-8} M.

(a) How does the equilibrium position change in the lungs?

(b) How does it change in O₂-deficient cells?

(c) Excessive vomiting may lead to metabolic alkalosis, in which [H3O+] in blood decreases. How does this condition affect the ability of Hb to transport O2?

(d) Diabetes mellitus may lead to metabolic acidosis, in which [H3O+] in blood increases. How does this condition affect the ability of Hb to transport O2?

16,183 Vitamin C (ascorbic acid, H₂C₆H₆O₆) is a weak diprotic acid. It is essential for the synthesis of collagen, the major protein in connective tissue. (a) If the pH of a 5.0% (w/v) solution of vitamin C in water is 2.77, calculate the K_{a1} of vitamin C. (b) The vitamin is also taken as its sodium salt. What is the pH of a 10.0 g/L solution of sodium ascorbate (NaAsc)?

18.184 Because of the behavior of their R groups in water, lysine is called a basic amino acid and aspartic acid an acidic amino acid. Write balanced equations that demonstrate this behavior.

18.185 A solution of propanoic acid (CH3CH2COOH), made by dissolving 7.500 g in sufficient water to make 100.0 mL, has a freezing point of -1.890°C.

(a) Calculate the molarity of the solution.

(b) Calculate the molarity of the propanoate ion. (Assume the molarity of the solution equals the molality.)

(c) Calculate the percent dissociation of propanoic acid.

18.186 Quinine (C20H24N2O2; see below) is a natural product with antimalarial properties that saved thousands during construction of the Panama Canal. It stands as a classic example of the medicinal wealth of tropical forests. Both N atoms are basic, but the N (colored) of the 3° amine group is far more basic (p $K_b = 5.1$) than the N within the aromatic ring system ($pK_b = 9.7$).

(a) Quinine is not very soluble in water: a saturated solution is only 1.6×10^{-3} M. What is the pH of this solution?

(b) Show that the aromatic N contributes negligibly to the pH of the solution.

(c) Because of its low solubility as a free base in water, quinine is given as an amine salt. For instance, quinine hydrochloride (C20H24N2O2·HCl) is about 120 times more soluble in water than quinine. What is the pH of 0.53 M quinine hydrochloride? (d) An antimalarial concentration in water is 1.5% quinine hy-

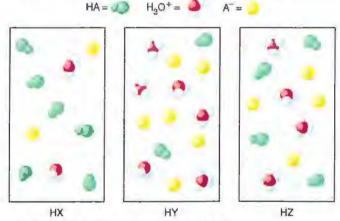
drochloride by mass (d = 1.0 g/mL). What is the pH? 18.187 Drinking water is often disinfected with chlorine gas, which hydrolyzes to form hypochlorous acid (HClO), a weak acid but powerful disinfectant:

 $Cl_2(aq) + 2H_2O(l) \longrightarrow HClO(aq) + H_3O^+(aq) + Cl^-(aq)$

The fraction of HOCl in solution is defined as

(a) What is the fraction of HOCl at pH 7.00 (K_a of HClO = 2.9×10^{-8})? (b) What is the fraction at pH 10.00?

18.188 The following scenes represent three weak acids HA (where A = X, Y, or Z) dissolved in water (H_2O is not shown):



(a) Rank the acids in order of increasing Ka.

(b) Rank the acids in order of increasing pK_a .

(c) Rank the conjugate bases in order of increasing pK_b .

(d) What is the percent dissociation of HX?

(e) If equimolar amounts of the sodium salts of the acids (NaX, NaY, and NaZ) were dissolved in water, which solution would have the highest pOH? The lowest pH?

CHEMISTRY

The Molecular Nature of Matter and Change

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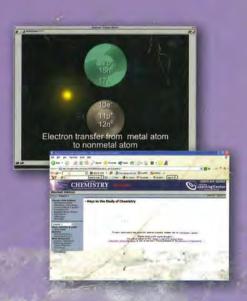
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MODERN ANALYTICAL CHEMISTRY

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This book is printed on acid-free paper.

1 2 3 4 5 6 7 8 9 0 KGP/KGP 0 9 8 7 6 5 4 3 2 1 0

ISBN 0-07-237547-7

Vice president and editorial director: Kevin T. Kane

Publisher: James M. Smith

Sponsoring editor: *Kent A. Peterson* Editorial assistant: *Jennifer L. Bensink*

Developmental editor: Shirley R. Oberbroeckling Senior marketing manager: Martin J. Lange Senior project manager: Jayne Klein Production supervisor: Laura Fuller

Coordinator of freelance design: Michelle D. Whitaker Senior photo research coordinator: Lori Hancock Senior supplement coordinator: Audrey A. Reiter

Compositor: *Shepherd, Inc.* Typeface: 10/12 Minion

Printer: Quebecor Printing Book Group/Kingsport

Freelance cover/interior designer: Elise Lansdon Cover image: © George Diebold/The Stock Market Photo research: Roberta Spieckerman Associates

Colorplates: Colorplates 1–6, 8, 10: © David Harvey/Marilyn E. Culler, photographer; Colorplate 7: Richard Megna/Fundamental Photographs; Colorplate 9: © Alfred Pasieka/Science Photo Library/Photo Researchers, Inc.; Colorplate 11: From H. Black, *Environ. Sci. Technol.*, **1996,** *30*, 124A. Photos courtesy D. Pesiri and W. Tumas, Los Alamos National Laboratory; Colorplate 12: Courtesy of Hewlett-Packard Company; Colorplate 13: © David Harvey.

Library of Congress Cataloging-in-Publication Data

Harvey, David, 1956-

Modern analytical chemistry / David Harvey. — 1st ed.

p. cm

Includes bibliographical references and index.

ISBN 0-07-237547-7

1. Chemistry, Analytic. I. Title.

QD75.2.H374 2000

543—dc21 99–15120 CIP

INTERNATIONAL EDITION ISBN 0-07-116953-9

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Chapter 2

Basic Tools of Analytical Chemistry

n the chapters that follow we will learn about the specifics of analytical chemistry. In the process we will ask and answer questions such as "How do we treat experimental data?" "How do we ensure that our results are accurate?" "How do we obtain a representative sample?" and "How do we select an appropriate analytical technique?" Before we look more closely at these and other questions, we will first review some basic numerical and experimental tools of importance to analytical chemists.

2A Nu

Numbers in Analytical Chemistry

Analytical chemistry is inherently a quantitative science. Whether determining the concentration of a species in a solution, evaluating an equilibrium constant, measuring a reaction rate, or drawing a correlation between a compound's structure and its reactivity, analytical chemists make measurements and perform calculations. In this section we briefly review several important topics involving the use of numbers in analytical chemistry.

2A.I Fundamental Units of Measure

Imagine that you find the following instructions in a laboratory procedure: "Transfer 1.5 of your sample to a 100 volumetric flask, and dilute to volume." How do you do this? Clearly these instructions are incomplete since the units of measurement are not stated. Compare this with a complete instruction: "Transfer 1.5 g of your sample to a 100-mL volumetric flask, and dilute to volume." This is an instruction that you can easily follow.

Measurements usually consist of a unit and a number expressing the quantity of that unit. Unfortunately, many different units may be used to express the same physical measurement. For example, the mass of a sample weighing 1.5 g also may be expressed as 0.0033 lb or 0.053 oz. For consistency, and to avoid confusion, scientists use a common set of fundamental units, several of which are listed in Table 2.1. These units are called **SI units** after the *Système International d'Unités*. Other measurements are defined using these fundamental SI units. For example, we measure the quantity of heat produced during a chemical reaction in joules, (J), where

$$1 J = 1 \frac{m^2 kg}{s^2}$$

Table 2.2 provides a list of other important derived SI units, as well as a few commonly used non-SI units.

Chemists frequently work with measurements that are very large or very small. A mole, for example, contains 602,213,670,000,000,000,000,000 particles, and some analytical techniques can detect as little as 0.000000000000001 g of a compound. For simplicity, we express these measurements using **scientific notation**; thus, a mole contains 6.0221367×10^{23} particles, and the stated mass is 1×10^{-15} g. Sometimes it is preferable to express measurements without the exponential term, replacing it with a prefix. A mass of 1×10^{-15} g is the same as 1 femtogram. Table 2.3 lists other common prefixes.

SI units

Stands for *Système International d'Unités*. These are the internationally agreed on units for measurements.

scientific notation

A shorthand method for expressing very large or very small numbers by indicating powers of ten; for example, $1000 \text{ is } 1 \times 10^3$.

| Table 2.1 Fundamental SI Units | | | | |
|--------------------------------|----------|--------|--|--|
| Measurement | Unit | Symbol | | |
| mass | kilogram | kg | | |
| volume | liter | L | | |
| distance | meter | m | | |
| temperature | kelvin | K | | |
| time | second | S | | |
| current | ampere | Α | | |
| amount of substance | mole | mol | | |

| Table 2.2 Other SI and Non-SI Units | | | | |
|-------------------------------------|-------------------|--------|---|--|
| Measurement | Unit | Symbol | Equivalent SI units | |
| length | angstrom | Å | 1 $Å = 1 \times 10^{-10} \text{ m}$ | |
| force | newton | N | $1 N = 1 m \cdot kg/s^2$ | |
| pressure | pascal | Pa | 1 Pa = 1 N/m ² = 1 kg/(m • s^2) | |
| | atmosphere | atm | 1 atm = 101,325 Pa | |
| energy, work, heat | joule | J | $1 J = 1 N \cdot m = 1 m^2 \cdot kg/s^2$ | |
| power | watt | W | 1 W = 1 J/s = 1 $m^2 \cdot kg/s^3$ | |
| charge | coulomb | C | 1 C = 1 A • s | |
| potential | volt | V | $1 V = 1 W/A = 1 m^2 \cdot kg/(s^3 \cdot A)$ | |
| temperature | degree Celsius | °C | °C = K – 273.15 | |
| | degree Fahrenheit | °F | $^{\circ}F = 1.8(K - 273.15) + 32$ | |

| Table 2.3 | Table 2.3 Common Prefixes for Exponentia Notation | | | |
|-------------------|---|--------|--|--|
| Exponential | Prefix | Symbol | | |
| 10 ¹² | tera | Т | | |
| 10 ⁹ | giga | G | | |
| 10 ⁶ | mega | M | | |
| 10 ³ | kilo | k | | |
| 10 ⁻¹ | deci | d | | |
| 10-2 | centi | С | | |
| 10 ⁻³ | milli | m | | |
| 10 ⁻⁶ | micro | μ | | |
| 10 ⁻⁹ | nano | n | | |
| 10 ⁻¹² | pico | р | | |
| 10 ⁻¹⁵ | femto | f | | |
| 10 ⁻¹⁸ | atto | a | | |

2A.2 Significant Figures

Recording a measurement provides information about both its magnitude and uncertainty. For example, if we weigh a sample on a balance and record its mass as 1.2637 g, we assume that all digits, except the last, are known exactly. We assume that the last digit has an uncertainty of at least ± 1 , giving an absolute uncertainty of at least ± 0.0001 g, or a relative uncertainty of at least

$$\frac{\pm 0.0001 \text{ g}}{1.2637 \text{ g}} \times 100 = \pm 0.0079\%$$

Significant figures are a reflection of a measurement's uncertainty. The number of significant figures is equal to the number of digits in the measurement, with the exception that a zero (0) used to fix the location of a decimal point is not considered significant. This definition can be ambiguous. For example, how many significant figures are in the number 100? If measured to the nearest hundred, then there is one significant figure. If measured to the nearest ten, however, then two

significant figures

The digits in a measured quantity, including all digits known exactly and one digit (the last) whose quantity is uncertain.

significant figures are included. To avoid ambiguity we use scientific notation. Thus, 1×10^2 has one significant figure, whereas 1.0×10^2 has two significant figures.

For measurements using logarithms, such as pH, the number of significant figures is equal to the number of digits to the right of the decimal, including all zeros. Digits to the left of the decimal are not included as significant figures since they only indicate the power of 10. A pH of 2.45, therefore, contains two significant figures.

Exact numbers, such as the stoichiometric coefficients in a chemical formula or reaction, and unit conversion factors, have an infinite number of significant figures. A mole of CaCl₂, for example, contains exactly two moles of chloride and one mole of calcium. In the equality

$$1000 \text{ mL} = 1 \text{ L}$$

both numbers have an infinite number of significant figures.

Recording a measurement to the correct number of significant figures is important because it tells others about how precisely you made your measurement. For example, suppose you weigh an object on a balance capable of measuring mass to the nearest ± 0.1 mg, but record its mass as 1.762 g instead of 1.7620 g. By failing to record the trailing zero, which is a significant figure, you suggest to others that the mass was determined using a balance capable of weighing to only the nearest ± 1 mg. Similarly, a buret with scale markings every 0.1 mL can be read to the nearest ± 0.01 mL. The digit in the hundredth's place is the least significant figure since we must estimate its value. Reporting a volume of 12.241 mL implies that your buret's scale is more precise than it actually is, with divisions every 0.01 mL.

Significant figures are also important because they guide us in reporting the result of an analysis. When using a measurement in a calculation, the result of that calculation can never be more certain than that measurement's uncertainty. Simply put, the result of an analysis can never be more certain than the least certain measurement included in the analysis.

As a general rule, mathematical operations involving addition and subtraction are carried out to the last digit that is significant for all numbers included in the calculation. Thus, the sum of 135.621, 0.33, and 21.2163 is 157.17 since the last digit that is significant for all three numbers is in the hundredth's place.

$$135.621 + 0.33 + 21.2163 = 157.1673 = 157.17$$

When multiplying and dividing, the general rule is that the answer contains the same number of significant figures as that number in the calculation having the fewest significant figures. Thus,

$$\frac{22.91 \times 0.152}{16.302} = 0.21361 = 0.214$$

It is important to remember, however, that these rules are generalizations. What is conserved is not the number of significant figures, but absolute uncertainty when adding or subtracting, and relative uncertainty when multiplying or dividing. For example, the following calculation reports the answer to the correct number of significant figures, even though it violates the general rules outlined earlier.

$$\frac{101}{99} = 1.02$$

Since the relative uncertainty in both measurements is roughly 1% ($101 \pm 1, 99 \pm 1$), the relative uncertainty in the final answer also must be roughly 1%. Reporting the answer to only two significant figures (1.0), as required by the general rules, implies a relative uncertainty of 10%. The correct answer, with three significant figures, yields the expected relative uncertainty. Chapter 4 presents a more thorough treatment of uncertainty and its importance in reporting the results of an analysis.

Finally, to avoid "round-off" errors in calculations, it is a good idea to retain at least one extra significant figure throughout the calculation. This is the practice adopted in this textbook. Better yet, invest in a good scientific calculator that allows you to perform lengthy calculations without recording intermediate values. When the calculation is complete, the final answer can be rounded to the correct number of significant figures using the following simple rules.

- 1. Retain the least significant figure if it and the digits that follow are less than halfway to the next higher digit; thus, rounding 12.442 to the nearest tenth gives 12.4 since 0.442 is less than halfway between 0.400 and 0.500.
- 2. Increase the least significant figure by 1 if it and the digits that follow are more than halfway to the next higher digit; thus, rounding 12.476 to the nearest tenth gives 12.5 since 0.476 is more than halfway between 0.400 and 0.500.
- 3. If the least significant figure and the digits that follow are exactly halfway to the next higher digit, then round the least significant figure to the nearest even number; thus, rounding 12.450 to the nearest tenth gives 12.4, but rounding 12.550 to the nearest tenth gives 12.6. Rounding in this manner prevents us from introducing a bias by always rounding up or down.

2B Units for Expressing Concentration

Concentration is a general measurement unit stating the amount of solute present in a known amount of solution

Concentration =
$$\frac{\text{amount of solute}}{\text{amount of solution}}$$
 2.1

Although the terms "solute" and "solution" are often associated with liquid samples, they can be extended to gas-phase and solid-phase samples as well. The actual units for reporting concentration depend on how the amounts of solute and solution are measured. Table 2.4 lists the most common units of concentration.

2B.I Molarity and Formality

Both molarity and formality express concentration as moles of solute per liter of solution. There is, however, a subtle difference between molarity and formality. **Molarity** is the concentration of a particular chemical species in solution. **Formality**, on the other hand, is a substance's total concentration in solution without regard to its specific chemical form. There is no difference between a substance's molarity and formality if it dissolves without dissociating into ions. The molar concentration of a solution of glucose, for example, is the same as its formality.

For substances that ionize in solution, such as NaCl, molarity and formality are different. For example, dissolving 0.1 mol of NaCl in 1 L of water gives a solution containing 0.1 mol of Na⁺ and 0.1 mol of Cl⁻. The molarity of NaCl, therefore, is zero since there is essentially no undissociated NaCl in solution. The solution,

concentration

An expression stating the relative amount of solute per unit volume or unit mass of solution.

molarity

The number of moles of solute per liter of solution (M).

formality

The number of moles of solute, regardless of chemical form, per liter of solution (F).

| Table 2.4 Common Units for Reporting Concentration | | | | |
|--|--|--------|--|--|
| Name | Units ^a | Symbol | | |
| molarity | moles solute liters solution | М | | |
| formality | number FWs solute liters solution | F | | |
| normality | number EWs solute liters solution | N | | |
| molality | moles solute kg solvent | m | | |
| weight % | g solute 100 g solution | % w/w | | |
| volume % | mL solute 100 mL solution | % v/v | | |
| weight-to-volume % | g solute | % w/v | | |
| parts per million | g solute 10 ⁶ g solution | ppm | | |
| parts per billion | g solute 10 ⁹ g solution | ppb | | |
| | | | | |

^aFW = formula weight; EW = equivalent weight.

instead, is 0.1 M in Na⁺ and 0.1 M in Cl⁻. The formality of NaCl, however, is 0.1 F because it represents the total amount of NaCl in solution. The rigorous definition of molarity, for better or worse, is largely ignored in the current literature, as it is in this text. When we state that a solution is 0.1 M NaCl we understand it to consist of Na⁺ and Cl⁻ ions. The unit of formality is used only when it provides a clearer description of solution chemistry.

Molar concentrations are used so frequently that a symbolic notation is often used to simplify its expression in equations and writing. The use of square brackets around a species indicates that we are referring to that species' molar concentration. Thus, [Na⁺] is read as the "molar concentration of sodium ions."

2B.2 Normality

Normality is an older unit of concentration that, although once commonly used, is frequently ignored in today's laboratories. Normality is still used in some handbooks of analytical methods, and, for this reason, it is helpful to understand its meaning. For example, normality is the concentration unit used in *Standard Methods for the Examination of Water and Wastewater*, 1 a commonly used source of analytical methods for environmental laboratories.

Normality makes use of the chemical equivalent, which is the amount of one chemical species reacting stoichiometrically with another chemical species. Note that this definition makes an equivalent, and thus normality, a function of the chemical reaction in which the species participates. Although a solution of $\rm H_2SO_4$ has a fixed molarity, its normality depends on how it reacts.

normality

The number of equivalents of solute per liter of solution (N).

The number of **equivalents**, *n*, is based on a reaction unit, which is that part of a chemical species involved in a reaction. In a precipitation reaction, for example, the reaction unit is the charge of the cation or anion involved in the reaction; thus for the reaction

$$Pb^{2+}(aq) + 2I^{-}(aq) \rightleftharpoons PbI_{2}(s)$$

n=2 for Pb²⁺ and n=1 for I⁻. In an acid–base reaction, the reaction unit is the number of H⁺ ions donated by an acid or accepted by a base. For the reaction between sulfuric acid and ammonia

$$H_2SO_4(aq) + 2NH_3(aq) \rightleftharpoons 2NH_4^+(aq) + SO_4^{2-}(aq)$$

we find that n = 2 for H_2SO_4 and n = 1 for NH_3 . For a complexation reaction, the reaction unit is the number of electron pairs that can be accepted by the metal or donated by the ligand. In the reaction between Ag^+ and NH_3

$$Ag^{+}(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^{+}(aq)$$

the value of n for Ag^+ is 2 and that for NH_3 is 1. Finally, in an oxidation–reduction reaction the reaction unit is the number of electrons released by the reducing agent or accepted by the oxidizing agent; thus, for the reaction

$$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightleftharpoons Sn^{4+}(aq) + 2Fe^{2+}(aq)$$

n = 1 for Fe³⁺ and n = 2 for Sn²⁺. Clearly, determining the number of equivalents for a chemical species requires an understanding of how it reacts.

Normality is the number of **equivalent weights** (EW) per unit volume and, like formality, is independent of speciation. An equivalent weight is defined as the ratio of a chemical species' **formula weight** (FW) to the number of its equivalents

$$EW = \frac{FW}{n}$$

Consequently, the following simple relationship exists between normality and molarity.

$$N = n \times M$$

Example 2.1 illustrates the relationship among chemical reactivity, equivalent weight, and normality.

EXAMPLE 2.1

Calculate the equivalent weight and normality for a solution of $6.0~M~H_3PO_4$ given the following reactions:

(a)
$$H_3PO_4(aq) + 3OH^-(aq) \rightleftharpoons PO_4^{3-}(aq) + 3H_2O(\ell)$$

(b)
$$H_3PO_4(aq) + 2NH_3(aq) \rightleftharpoons HPO_4^{2-}(aq) + 2NH_4^{+}(aq)$$

(c)
$$H_3PO_4(aq) + F^-(aq) \rightleftharpoons H_2PO_4^-(aq) + HF(aq)$$

SOLUTION

For phosphoric acid, the number of equivalents is the number of H⁺ ions donated to the base. For the reactions in (a), (b), and (c) the number of equivalents are 3, 2, and 1, respectively. Thus, the calculated equivalent weights and normalities are

equivalent

The moles of a species that can donate one reaction unit.

equivalent weight

The mass of a compound containing one equivalent (EW).

formula weight

The mass of a compound containing one mole (FW).

(a)
$$EW = \frac{FW}{n} = \frac{97.994}{3} = 32.665$$
 $N = n \times M = 3 \times 6.0 = 18 \text{ N}$
(b) $EW = \frac{FW}{n} = \frac{97.994}{2} = 48.997$ $N = n \times M = 2 \times 6.0 = 12 \text{ N}$
(c) $EW = \frac{FW}{n} = \frac{97.994}{1} = 97.994$ $N = n \times M = 1 \times 6.0 = 6.0 \text{ N}$

b) EW =
$$\frac{\text{FW}}{n} = \frac{97.994}{2} = 48.997$$
 N = $n \times M = 2 \times 6.0 = 12 \text{ N}$

(c) EW =
$$\frac{\text{FW}}{n} = \frac{97.994}{1} = 97.994$$
 N = $n \times M = 1 \times 6.0 = 6.0 \text{ N}$

molality

The number of moles of solute per kilogram of solvent (m).

weight percent

Grams of solute per 100 g of solution. (% w/w).

volume percent

Milliliters of solute per 100 mL of solution (% v/v).

weight-to-volume percent

Grams of solute per 100 mL of solution (% w/v).

parts per million

Micrograms of solute per gram of solution; for aqueous solutions the units are often expressed as milligrams of solute per liter of solution (ppm).

parts per billion

Nanograms of solute per gram of solution; for aqueous solutions the units are often expressed as micrograms of solute per liter of solution (ppb).

2B.3 Molality

Molality is used in thermodynamic calculations where a temperature independent unit of concentration is needed. Molarity, formality and normality are based on the volume of solution in which the solute is dissolved. Since density is a temperature dependent property a solution's volume, and thus its molar, formal and normal concentrations, will change as a function of its temperature. By using the solvent's mass in place of its volume, the resulting concentration becomes independent of temperature.

2B.4 Weight, Volume, and Weight-to-Volume Ratios

Weight percent (% w/w), volume percent (% v/v) and weight-to-volume percent (% w/v) express concentration as units of solute per 100 units of sample. A solution in which a solute has a concentration of 23% w/v contains 23 g of solute per 100 mL of solution.

Parts per million (ppm) and parts per billion (ppb) are mass ratios of grams of solute to one million or one billion grams of sample, respectively. For example, a steel that is 450 ppm in Mn contains 450 µg of Mn for every gram of steel. If we approximate the density of an aqueous solution as 1.00 g/mL, then solution concentrations can be expressed in parts per million or parts per billion using the following relationships.

$$ppm = \frac{mg}{liter} = \frac{\mu g}{mL}$$

$$ppb = \frac{\mu g}{liter} = \frac{ng}{mL}$$

For gases a part per million usually is a volume ratio. Thus, a helium concentration of 6.3 ppm means that one liter of air contains 6.3 µL of He.

2B.5 Converting Between Concentration Units

The units of concentration most frequently encountered in analytical chemistry are molarity, weight percent, volume percent, weight-to-volume percent, parts per million, and parts per billion. By recognizing the general definition of concentration given in equation 2.1, it is easy to convert between concentration units.

EXAMPLE 2.2

A concentrated solution of aqueous ammonia is 28.0% w/w NH₃ and has a density of 0.899 g/mL. What is the molar concentration of NH₃ in this solution?

SOLUTION

$$\frac{28.0 \text{ g NH}_3}{100 \text{ g solution}} \times \frac{0.899 \text{ g solution}}{\text{mL solution}} \times \frac{1 \text{ mole NH}_3}{17.04 \text{ g NH}_3} \times \frac{1000 \text{ mL}}{\text{liter}} = 14.8 \text{ M}$$

EXAMPLE 2.3

The maximum allowed concentration of chloride in a municipal drinking water supply is 2.50×10^2 ppm Cl⁻. When the supply of water exceeds this limit, it often has a distinctive salty taste. What is this concentration in moles Cl⁻/liter?

SOLUTION

$$\frac{2.50 \times 10^{2} \text{ mg Cl}^{-}}{\text{L}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mole Cl}^{-}}{35.453 \text{ g Cl}^{-}} = 7.05 \times 10^{-3} \text{ M}$$

2B.6 p-Functions

Sometimes it is inconvenient to use the concentration units in Table 2.4. For example, during a reaction a reactant's concentration may change by many orders of magnitude. If we are interested in viewing the progress of the reaction graphically, we might wish to plot the reactant's concentration as a function of time or as a function of the volume of a reagent being added to the reaction. Such is the case in Figure 2.1, where the molar concentration of H⁺ is plotted (*y*-axis on left side of figure) as a function of the volume of NaOH added to a solution of HCl. The initial [H⁺] is 0.10 M, and its concentration after adding 75 mL of NaOH is 5.0×10^{-13} M. We can easily follow changes in the [H⁺] over the first 14 additions of NaOH. For the last ten additions of NaOH, however, changes in the [H⁺] are too small to be seen.

When working with concentrations that span many orders of magnitude, it is often more convenient to express the concentration as a **p-function**. The p-function of a number X is written as pX and is defined as

$$pX = -\log(X)$$

Thus, the pH of a solution that is 0.10 M H⁺ is

$$pH = -log[H^+] = -log(0.10) = 1.00$$

and the pH of 5.0×10^{-13} M H⁺ is

$$pH = -log[H^+] = -log(5.0 \times 10^{-13}) = 12.30$$

Figure 2.1 shows how plotting pH in place of [H⁺] provides more detail about how the concentration of H⁺ changes following the addition of NaOH.

EXAMPLE 2.4

What is pNa for a solution of 1.76×10^{-3} M Na₃PO₄?

SOLUTION

Since each mole of Na₃PO₄ contains three moles of Na⁺, the concentration of Na⁺ is

$$[\text{Na}^+] = \frac{3 \text{ mol Na}^+}{\text{mol Na}_3 \text{PO}_4} \times 1.76 \times 10^{-3} \text{ M} = 5.28 \times 10^{-3} \text{ M}$$

and pNa is

$$pNa = -log[Na^+] = -log(5.28 \times 10^{-3}) = 2.277$$

p-function

A function of the form p*X*, where $pX = -\log(X)$.

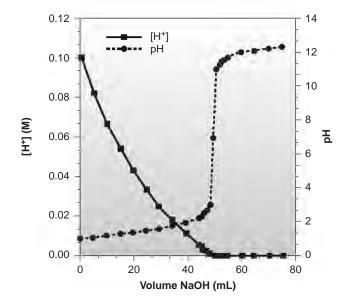
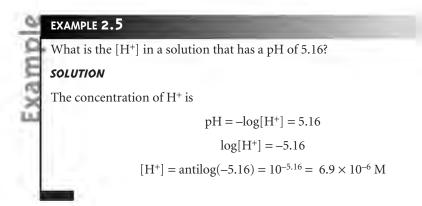


Figure 2.1Graph of [H+] versus volume of NaOH and pH versus volume of NaOH for the reaction of 0.10 M HCl with 0.10 M NaOH.



2C Stoichiometric Calculations

A balanced chemical reaction indicates the quantitative relationships between the moles of reactants and products. These stoichiometric relationships provide the basis for many analytical calculations. Consider, for example, the problem of determining the amount of oxalic acid, $H_2C_2O_4$, in rhubarb. One method for this analysis uses the following reaction in which we oxidize oxalic acid to CO_2 .

$$2Fe^{3+}(aq) + H_2C_2O_4(aq) + 2H_2O(\ell) \rightarrow 2Fe^{2+}(aq) + 2CO_2(g) + 2H_3O^+(aq)$$
 2.2

The balanced chemical reaction provides the stoichiometric relationship between the moles of Fe³⁺ used and the moles of oxalic acid in the sample being analyzed—specifically, one mole of oxalic acid reacts with two moles of Fe³⁺. As shown in Example 2.6, the balanced chemical reaction can be used to determine the amount of oxalic acid in a sample, provided that information about the number of moles of Fe³⁺ is known.

EXAMPLE 2.6

The amount of oxalic acid in a sample of rhubarb was determined by reacting with Fe³⁺ as outlined in reaction 2.2. In a typical analysis, the oxalic acid in 10.62 g of rhubarb was extracted with a suitable solvent. The complete oxidation of the oxalic acid to CO_2 required 36.44 mL of 0.0130 M Fe³⁺. What is the weight percent of oxalic acid in the sample of rhubarb?

SOLUTION

We begin by calculating the moles of Fe³⁺ used in the reaction

$$\frac{0.0130 \text{ mol Fe}^{3+}}{L} \times 0.03644 \text{ L} = 4.737 \times 10^{-4} \text{ mol Fe}^{3+}$$

The moles of oxalic acid reacting with the Fe³⁺, therefore, is

$$4.737 \times 10^{-4} \text{ mol Fe}^{3+} \times \frac{1 \text{ mol } C_2 H_2 O_4}{2 \text{ mol Fe}^{3+}} = 2.369 \times 10^{-4} \text{ mol } C_2 H_2 O_4$$

Converting moles of oxalic acid to grams of oxalic acid

$$2.369 \times 10^{-4} \text{ mol } C_2H_2O_4 \times \frac{90.03 \text{ g } C_2H_2O_4}{\text{mol } C_2H_2O_4} = 2.132 \times 10^{-2} \text{ g oxalic acid}$$

and converting to weight percent gives the concentration of oxalic acid in the sample of rhubarb as

$$\frac{2.132 \times 10^{-2} \text{ g C}_2 \text{H}_2 \text{O}_4}{10.62 \text{ g rhubarb}} \times 100 = 0.201\% \text{ w/w C}_2 \text{H}_2 \text{O}_4$$

In the analysis described in Example 2.6 oxalic acid already was present in the desired form. In many analytical methods the compound to be determined must be converted to another form prior to analysis. For example, one method for the quantitative analysis of tetraethylthiuram disulfide ($C_{10}H_{20}N_2S_4$), the active ingredient in the drug Antabuse (disulfiram), requires oxidizing the S to SO_2 , bubbling the SO_2 through H_2O_2 to produce H_2SO_4 , followed by an acid–base titration of the H_2SO_4 with NaOH. Although we can write and balance chemical reactions for each of these steps, it often is easier to apply the principle of the conservation of reaction units.

A reaction unit is that part of a chemical species involved in a reaction. Consider, for example, the general unbalanced chemical reaction

$$A + B \rightarrow Products$$

Conservation of reaction units requires that the number of reaction units associated with the reactant A equal the number of reaction units associated with the reactant B. Translating the previous statement into mathematical form gives

Number of reaction units per A
$$\times$$
 moles A = number of reaction units per B \times moles B

If we know the moles of A and the number of reaction units associated with A and B, then we can calculate the moles of B. Note that a conservation of reaction units, as defined by equation 2.3, can only be applied between two species. There are five important principles involving a conservation of reaction units: mass, charge, protons, electron pairs, and electrons.

2C.I Conservation of Mass

The easiest principle to appreciate is conservation of mass. Except for nuclear reactions, an element's total mass at the end of a reaction must be the same as that present at the beginning of the reaction; thus, an element serves as the most fundamental reaction unit. Consider, for example, the combustion of butane to produce CO_2 and H_2O , for which the unbalanced reaction is

$$C_4H_{10}(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$$

All the carbon in CO_2 comes from the butane, thus we can select carbon as a reaction unit. Since there are four carbon atoms in butane, and one carbon atom in CO_2 , we write

$$4 \times \text{moles C}_4H_{10} = 1 \times \text{moles CO}_2$$

Hydrogen also can be selected as a reaction unit since all the hydrogen in butane ends up in the H_2O produced during combustion. Thus, we can write

$$10 \times \text{moles C}_4H_{10} = 2 \times \text{moles H}_2O$$

Although the mass of oxygen is conserved during the reaction, we cannot apply equation 2.3 because the O_2 used during combustion does not end up in a single product.

Conservation of mass also can, with care, be applied to groups of atoms. For example, the ammonium ion, NH_4^+ , can be precipitated as $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. Selecting NH_4^+ as the reaction unit gives

$$2 \times \text{moles Fe}(NH_4)_2(SO_4)_2 \cdot 6H_2O = 1 \times \text{moles NH}_4^+$$

2C.2 Conservation of Charge

The stoichiometry between two reactants in a precipitation reaction is governed by a conservation of charge, requiring that the total cation charge and the total anion charge in the precipitate be equal. The reaction units in a precipitation reaction, therefore, are the absolute values of the charges on the cation and anion that make up the precipitate. Applying equation 2.3 to a precipitate of $Ca_3(PO_4)_2$ formed from the reaction of Ca^{2+} and PO_4^{3-} , we write

$$2 \times \text{moles Ca}^{2+} = 3 \times \text{moles PO}_4^{3-}$$

2C.3 Conservation of Protons

In an acid–base reaction, the reaction unit is the proton. For an acid, the number of reaction units is given by the number of protons that can be donated to the base; and for a base, the number of reaction units is the number of protons that the base can accept from the acid. In the reaction between H₃PO₄ and NaOH, for example, the weak acid H₃PO₄ can donate all three of its protons to NaOH, whereas the strong base NaOH can accept one proton. Thus, we write

$$3 \times \text{moles H}_3\text{PO}_4 = 1 \times \text{moles NaOH}$$

Care must be exercised in determining the number of reaction units associated with the acid and base. The number of reaction units for an acid, for instance, depends not on how many acidic protons are present, but on how many

of the protons are capable of reacting with the chosen base. In the reaction between H_3PO_4 and NH_3

$$H_3PO_4(aq) + 2NH_3(aq) \rightleftharpoons HPO_4^-(aq) + 2NH_4^+(aq)$$

a conservation of protons requires that

$$2 \times \text{moles H}_3\text{PO}_4 = \text{moles of NH}_3$$

2C.4 Conservation of Electron Pairs

In a complexation reaction, the reaction unit is an electron pair. For the metal, the number of reaction units is the number of coordination sites available for binding ligands. For the ligand, the number of reaction units is equivalent to the number of electron pairs that can be donated to the metal. One of the most important analytical complexation reactions is that between the ligand ethylenediaminetetracetic acid (EDTA), which can donate 6 electron pairs and 6 coordinate metal ions, such as Cu²⁺; thus

$$6 \times \text{mole Cu}^{2+} = 6 \times \text{moles EDTA}$$

2C.5 Conservation of Electrons

In a redox reaction, the reaction unit is an electron transferred from a reducing agent to an oxidizing agent. The number of reaction units for a reducing agent is equal to the number of electrons released during its oxidation. For an oxidizing agent, the number of reaction units is given by the number of electrons needed to cause its reduction. In the reaction between Fe³⁺ and oxalic acid (reaction 2.2), for example, Fe³⁺ undergoes a 1-electron reduction. Each carbon atom in oxalic acid is initially present in a +3 oxidation state, whereas the carbon atom in CO_2 is in a +4 oxidation state. Thus, we can write

$$1 \times \text{moles Fe}^{3+} = 2 \times \text{moles of H}_2\text{C}_2\text{O}_4$$

Note that the moles of oxalic acid are multiplied by 2 since there are two carbon atoms, each of which undergoes a 1-electron oxidation.

2C.6 Using Conservation Principles in Stoichiometry Problems

As shown in the following examples, the application of conservation principles simplifies stoichiometric calculations.

EXAMPLE 2.7

Rework Example 2.6 using conservation principles.

SOLUTION

Conservation of electrons for this redox reaction requires that

moles
$$Fe^{3+} = 2 \times moles H_2C_2O_4$$

which can be transformed by writing moles as the product of molarity and volume or as grams per formula weight.

$$M_{Fe^{3+}} \times V_{Fe^{3+}} = \frac{2 \times g H_2 C_2 O_4}{FW H_2 C_2 O_4}$$

Solving for g H₂C₂O₄ gives

$$\frac{M_{Fe^{3+}} \times V_{Fe^{3+}} \times FW \text{ H}_2\text{C}_2\text{O}_4}{2} = \frac{(0.0130 \text{ M})(0.03644 \text{ L})(90.03 \text{ g/mole})}{2}$$
$$= 2.132 \times 10^{-2} \text{ g H}_2\text{C}_2\text{O}_4$$

and the weight percent oxalic acid is

$$\frac{2.132 \times 10^{-2} \text{ g C}_2 \text{H}_2 \text{O}_4}{10.62 \text{ g rhubarb}} \times 100 = 0.201\% \text{ w/w C}_2 \text{H}_2 \text{O}_4$$

EXAMPLE 2.8

One quantitative analytical method for tetraethylthiuram disulfide, $C_{10}H_{20}N_2S_4$ (Antabuse), requires oxidizing the sulfur to SO_2 , and bubbling the resulting SO_2 through H_2O_2 to produce H_2SO_4 . The H_2SO_4 is then reacted with NaOH according to the reaction

$$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(\ell)$$

Using appropriate conservation principles, derive an equation relating the moles of $C_{10}H_{20}N_2S_4$ to the moles of NaOH. What is the weight percent $C_{10}H_{20}N_2S_4$ in a sample of Antabuse if the H_2SO_4 produced from a 0.4613-g portion reacts with 34.85 mL of 0.02500 M NaOH?

SOLUTION

The unbalanced reactions converting C₁₀H₂₀N₂S₄ to H₂SO₄ are

$$C_{10}H_{20}N_2S_4 \rightarrow SO_2$$

$$SO_2 \rightarrow H_2SO_4$$

Using a conservation of mass we have

$$4 \times \text{moles } C_{10}H_{20}N_2S_4 = \text{moles } SO_2 = \text{moles } H_2SO_4$$

A conservation of protons for the reaction of H₂SO₄ with NaOH gives

$$2 \times \text{moles H}_2SO_4 = \text{moles of NaOH}$$

Combining the two conservation equations gives the following stoichiometric equation between $C_{10}H_{20}N_2S_4$ and NaOH

$$8 \times \text{moles } C_{10}H_{20}N_2S_4 = \text{moles NaOH}$$

Now we are ready to finish the problem. Making appropriate substitutions for moles of $C_{10}H_{20}N_2S_4$ and moles of NaOH gives

$$\frac{8 \times g C_{10} H_{20} N_2 S_4}{FW C_{10} H_{20} N_2 S_4} = M_{NaOH} \times V_{NaOH}$$

Solving for g C₁₀H₂₀N₂S₄ gives

$$g C_{10}H_{20}N_2S_4 = \frac{1}{8} \times M_{NaOH} \times V_{NaOH} \times FW C_{10}H_{20}N_2S_4$$

$$\frac{1}{8}(0.02500 \text{ M})(0.03485 \text{ L})(296.54 \text{ g/mol}) = 0.032295 \text{ g C}_{10}\text{H}_{20}\text{N}_2\text{S}_4$$

The weight percent $C_{10}H_{20}N_2S_4$ in the sample, therefore, is

$$\frac{0.32295 \text{ g C}_{10} \text{H}_{20} \text{N}_2 \text{S}_4}{0.4613 \text{ g sample}} \times 100 = 7.001\% \text{ w/w C}_{10} \text{H}_{20} \text{N}_2 \text{S}_4$$

2D Basic Equipment and Instrumentation

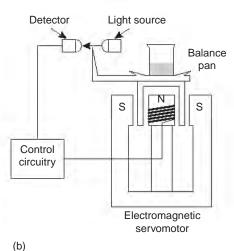
Measurements are made using appropriate equipment or instruments. The array of equipment and instrumentation used in analytical chemistry is impressive, ranging from the simple and inexpensive, to the complex and costly. With two exceptions, we will postpone the discussion of equipment and instrumentation to those chapters where they are used. The instrumentation used to measure mass and much of the equipment used to measure volume are important to all analytical techniques and are therefore discussed in this section.

2D.1 Instrumentation for Measuring Mass

An object's mass is measured using a **balance**. The most common type of balance is an electronic balance in which the balance pan is placed over an electromagnet (Figure 2.2). The sample to be weighed is placed on the sample pan, displacing the pan downward by a force equal to the product of the sample's mass and the acceleration due to gravity. The balance detects this downward movement and generates a counterbalancing force using an electromagnet. The current needed to produce this force is proportional to the object's mass. A typical electronic balance has a capacity of 100-200 g and can measure mass to the nearest ± 0.01 to ± 1 mg.

Another type of balance is the single-pan, unequal arm balance (Figure 2.3). In this mechanical balance the balance pan and a set of removable standard weights on one side of a beam are balanced against a fixed counterweight on the beam's other side. The beam itself is balanced on a fulcrum consisting of a sharp knife edge. Adding a sample to the balance pan tilts the beam away from its balance point. Selected standard weights are then removed until the beam is brought back into balance. The combined mass of the removed weights equals the sample's mass. The capacities and measurement limits of these balances are comparable to an electronic balance.

(a)



balanca

An apparatus used to measure mass.

Figure 2.2

(a) Photo of a typical electronic balance.
(b) Schematic diagram of electronic balance; adding a sample moves the balance pan down, allowing more light to reach the detector. The control circuitry directs the electromagnetic servomotor to generate an opposing force, raising the sample up until the original intensity of light at the detector is restored.

Photo courtesy of Fisher Scientific

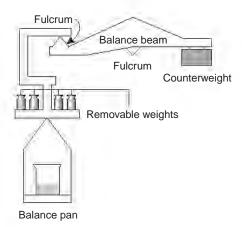


Figure 2.3Schematic diagram of single-arm mechanical balance.

The mass of a sample is determined by difference. If the material being weighed is not moisture-sensitive, a clean and dry container is placed on the balance. The mass of this container is called the tare. Most balances allow the tare to be automatically adjusted to read a mass of zero. The sample is then transferred to the container, the new mass is measured and the sample's mass determined by subtracting the tare. Samples that absorb moisture from the air are weighed differently. The sample is placed in a covered weighing bottle and their combined mass is determined. A portion of the sample is removed, and the weighing bottle and remaining sample are reweighed. The difference between the two masses gives the mass of the transferred sample.

Several important precautions help to minimize errors in measuring an object's mass. Balances should be placed on heavy surfaces to minimize the effect of vibrations in the surrounding environment and should be maintained in a level position. Analytical balances are sensitive enough that they can measure the mass of a fingerprint. For this reason, materials placed on a balance should normally be handled using tongs or laboratory tissues. Volatile liquid samples should be weighed in a covered container to avoid the loss of sample by evaporation. Air currents can significantly affect a sample's mass. To avoid air currents, the balance's glass doors should be closed, or the balance's wind shield should be in place. A sample that is cooler or warmer than the surrounding air will create convective air currents that adversely affect the measurement of its mass. Finally, samples dried in an oven should be stored in a desiccator to prevent them from reabsorbing moisture from the atmosphere.

2D.2 Equipment for Measuring Volume

Analytical chemists use a variety of glassware to measure volume, several examples of which are shown in Figure 2.4. The type of glassware used depends on how exact the volume needs to be. Beakers, dropping pipets, and graduated cylinders are used to measure volumes approximately, typically with errors of several percent.

Pipets and volumetric flasks provide a more accurate means for measuring volume. When filled to its calibration mark, a **volumetric flask** is designed to contain a specified volume of solution at a stated temperature, usually 20 °C. The actual vol-

volumetric flask

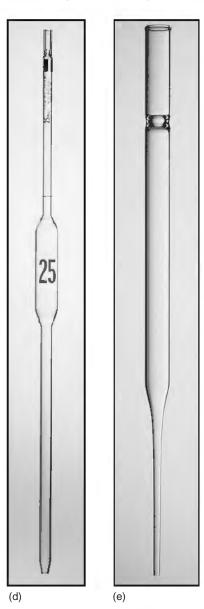
Glassware designed to contain a specific volume of solution when filled to its calibration mark.



Figure 2.4
Common examples of glassware used to measure volume:
(a) beaker; (b) graduated cylinder; (c) volumetric flask; (d) pipet; (e) dropping pipet.
Photos courtesy of Fisher Scientific.







ume contained by the volumetric flask is usually within 0.03–0.2% of the stated value. Volumetric flasks containing less than 100 mL generally measure volumes to the hundredth of a milliliter, whereas larger volumetric flasks measure volumes to the tenth of a milliliter. For example, a 10-mL volumetric flask contains 10.00 mL, but a 250-mL volumetric flask holds 250.0 mL (this is important when keeping track of significant figures).

Because a volumetric flask contains a solution, it is useful in preparing solutions with exact concentrations. The reagent is transferred to the volumetric flask, and enough solvent is added to dissolve the reagent. After the reagent is dissolved, additional solvent is added in several portions, mixing the solution after each addition. The final adjustment of volume to the flask's calibration mark is made using a dropping pipet. To complete the mixing process, the volumetric flask should be inverted at least ten times.

A **pipet** is used to deliver a specified volume of solution. Several different styles of pipets are available (Figure 2.5). Transfer pipets provide the most accurate means for delivering a known volume of solution; their volume error is similar to that from an equivalent volumetric flask. A 250-mL transfer pipet, for instance, will deliver 250.0 mL. To fill a transfer pipet, suction from a rubber bulb is used to pull the liquid up past the calibration mark (*never* use your mouth to suck a solution into a pipet). After replacing the bulb with your finger, the liquid's level is adjusted to the calibration mark, and the outside of the pipet is wiped dry. The pipet's contents are allowed to drain into the receiving container with the tip of the pipet touching the container walls. A small portion of the liquid remains in the pipet's tip and should not be blown out. Measuring pipets are used to deliver variable volumes, but with less accuracy than transfer pipets. With some measuring

pipetGlassware designed to deliver a specific volume of solution when filled to its calibration mark.



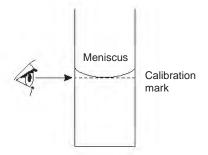


Figure 2.6Proper means of reading the meniscus on a volumetric flask or pipet.

pipets, delivery of the calibrated volume requires that any solution remaining in the tip be blown out. Digital pipets and syringes can be used to deliver volumes as small as a microliter.

Three important precautions are needed when working with pipets and volumetric flasks. First, the volume delivered by a pipet or contained by a volumetric flask assumes that the glassware is clean. Dirt and grease on the inner glass surface prevents liquids from draining evenly, leaving droplets of the liquid on the container's walls. For a pipet this means that the delivered volume is less than the calibrated volume, whereas drops of liquid above the calibration mark mean that a volumetric flask contains more than its calibrated volume. Commercially available cleaning solutions can be used to clean pipets and volumetric flasks.

Second, when filling a pipet or volumetric flask, set the liquid's level exactly at the calibration mark. The liquid's top surface is curved into a **meniscus**, the bottom of which should be exactly even with the glassware's calibration mark (Figure 2.6). The meniscus should be adjusted with the calibration mark at eye level to avoid parallax errors. If your eye level is above the calibration mark the pipet or volumetric flask will be overfilled. The pipet or volumetric flask will be underfilled if your eye level is below the calibration mark.

Finally, before using a pipet or volumetric flask you should rinse it with several small portions of the solution whose volume is being measured. This ensures that any residual liquid remaining in the pipet or volumetric flask is removed.

2D.3 Equipment for Drying Samples

Many materials need to be dried prior to their analysis to remove residual moisture. Depending on the material, heating to a temperature of 110–140 °C is usually sufficient. Other materials need to be heated to much higher temperatures to initiate thermal decomposition. Both processes can be accomplished using a laboratory oven capable of providing the required temperature.

Commercial laboratory ovens (Figure 2.7) are used when the maximum desired temperature is 160–325 °C (depending on the model). Some ovens include the ability to circulate heated air, allowing for a more efficient removal of moisture and shorter drying times. Other ovens provide a tight seal for the door, allowing the oven to be evacuated. In some situations a conventional laboratory oven can be replaced with a microwave oven. Higher temperatures, up to 1700° C, can be achieved using a muffle furnace (Figure 2.8).

After drying or decomposing a sample, it should be cooled to room temperature in a desiccator to avoid the readsorption of moisture. A **desiccator** (Figure 2.9) is a closed container that isolates the sample from the atmosphere. A drying agent, called a **desiccant**, is placed in the bottom of the container. Typical desiccants include calcium chloride and silica gel. A perforated plate sits above the desiccant, providing a shelf for storing samples. Some desiccators are equipped with stopcocks that allow them to be evacuated.

(b)





Figure 2.9(a) Desiccator. (b) Desiccator with stopcock for evacuating the desiccator. Photos courtesy of Fisher Scientific.

meniscus

The curved surface of a liquid contained in a tube.



Figure 2.7Conventional laboratory oven used for drying materials.



Figure 2.8
Example of a muffle furnace used for heating samples to maximum temperatures of 1100–1700 °C.
Courtesy of Fisher Scientific.

desiccator

A closed container containing a desiccant; used to store samples in a moisture-free environment.

desiccant

A drying agent.

2E Preparing Solutions

Preparing a solution of known concentration is perhaps the most common activity in any analytical lab. The method for measuring out the solute and solvent depend on the desired concentration units, and how exact the solution's concentration needs to be known. Pipets and volumetric flasks are used when a solution's concentration must be exact; graduated cylinders, beakers, and reagent bottles suffice when concentrations need only be approximate. Two methods for preparing solutions are described in this section.

2E.1 Preparing Stock Solutions

A **stock solution** is prepared by weighing out an appropriate portion of a pure solid or by measuring out an appropriate volume of a pure liquid and diluting to a known volume. Exactly how this is done depends on the required concentration units. For example, to prepare a solution with a desired molarity you would weigh out an appropriate mass of the reagent, dissolve it in a portion of solvent, and bring to the desired volume. To prepare a solution where the solute's concentration is given as a volume percent, you would measure out an appropriate volume of solute and add sufficient solvent to obtain the desired total volume.

stock solution

A solution of known concentration from which other solutions are prepared.

EXAMPLE 2.9

Describe how you would prepare the following three solutions: (a) 500 mL of approximately 0.20 M NaOH using solid NaOH; (b) 1 L of 150.0 ppm Cu²⁺ using Cu metal; and (c) 2 L of 4% v/v acetic acid using concentrated glacial acetic acid.

SOLUTION

(a) Since the concentration only needs to be known to two significant figures, the mass of NaOH and volume of solution do not need to be measured exactly. The desired mass of NaOH is

$$\frac{0.20 \text{ mol}}{L} \times \frac{40.0 \text{ g}}{\text{mol}} \times 0.50 \text{ L} = 4.0 \text{ g}$$

To prepare the solution we place 4.0 g of NaOH, weighed to the nearest tenth of a gram, in a bottle or beaker and add approximately 500 mL of water.

(b) Since the concentration of Cu²⁺ needs to be exact, the mass of Cu metal and the final solution volume must be measured exactly. The desired mass of Cu metal is

$$\frac{150.0 \text{ mg}}{L} \times 1.000 \text{ L} = 150.0 \text{ mg} = 0.1500 \text{ g}$$

To prepare the solution we measure out exactly 0.1500 g of Cu into a small beaker. To dissolve the Cu we add a small portion of concentrated HNO₃ and gently heat until it completely dissolves. The resulting solution is poured into a 1-L volumetric flask. The beaker is rinsed repeatedly with small portions of water, which are added to the volumetric flask. This process, which is called a **quantitative transfer**, ensures that the Cu²⁺ is completely transferred to the volumetric flask. Finally, additional water is added to the volumetric flask's calibration mark.

quantitative transfer

The process of moving a sample from one container to another in a manner that ensures all material is transferred. (c) The concentration of this solution is only approximate, so volumes do not need to be measured exactly. The necessary volume of glacial acetic acid is

$$\frac{4 \text{ mL CH}_3\text{COOH}}{100 \text{ mL}} \times 2000 \text{ mL} = 80 \text{ mL CH}_3\text{COOH}$$

To prepare the solution we use a graduated cylinder to transfer 80 mL of glacial acetic acid to a container that holds approximately 2 L, and we then add sufficient water to bring the solution to the desired volume.

2E.2 Preparing Solutions by Dilution

Solutions with small concentrations are often prepared by diluting a more concentrated stock solution. A known volume of the stock solution is transferred to a new container and brought to a new volume. Since the total amount of solute is the same before and after **dilution**, we know that

$$C_{\rm o} \times V_{\rm o} = C_{\rm d} \times V_{\rm d}$$
 2.4

where $C_{\rm o}$ is the concentration of the stock solution, $V_{\rm o}$ is the volume of the stock solution being diluted, $C_{\rm d}$ is the concentration of the dilute solution, and $V_{\rm d}$ is the volume of the dilute solution. Again, the type of glassware used to measure $V_{\rm o}$ and $V_{\rm d}$ depends on how exact the solution's concentration must be known.

EXAMPLE 2.10

A laboratory procedure calls for 250 mL of an approximately 0.10 M solution of NH₃. Describe how you would prepare this solution using a stock solution of concentrated NH₃ (14.8 M).

SOLUTION

Substituting known volumes in equation 2.4

$$14.8 \text{ M} \times V_{\text{o}} = 0.10 \text{ M} \times 0.25 \text{ L}$$

and solving for V_0 gives 1.69×10^{-3} L, or 1.7 mL. Since we are trying to make a solution that is approximately 0.10 M NH₃, we can measure the appropriate amount of concentrated NH₃ using a graduated cylinder, transfer the NH₃ to a beaker, and add sufficient water to bring the total solution volume to approximately 250 mL.

As shown in the following example, equation 2.4 also can be used to calculate a solution's original concentration using its known concentration after dilution.

EXAMPLE 2.11

A sample of an ore was analyzed for Cu²⁺ as follows. A 1.25-g sample of the ore was dissolved in acid and diluted to volume in a 250-mL volumetric flask. A 20-mL portion of the resulting solution was transferred by pipet to a 50-mL volumetric flask and diluted to volume. An analysis showed that the concentration of Cu²⁺ in the final solution was 4.62 ppm. What is the weight percent of Cu in the original ore?

dilution

The process of preparing a less concentrated solution from a more concentrated solution.



SOLUTION

Substituting known volumes (with significant figures appropriate for pipets and volumetric flasks) into equation 2.4

$$(ppm Cu^{2+})_o \times 20.00 \text{ mL} = 4.62 \text{ ppm} \times 50.00 \text{ mL}$$

and solving for $(ppm Cu^{2+})_0$ gives the original solution concentration as 11.55 ppm. To calculate the grams of Cu^{2+} we multiply this concentration by the total volume

$$\frac{11.55 \ \mu g \ Cu^{2+}}{mL} \times 250.0 \ mL \times \frac{1 \ g}{10^6 \ \mu g} = 2.888 \times 10^{-3} \ g \ Cu^{2+}$$

The weight percent Cu is then given by

$$\frac{2.888 \times 10^{-3} \text{ g Cu}^{2+}}{1.25 \text{ g sample}} \times 100 = 0.231\% \text{ w/w Cu}$$

2F The Laboratory Notebook

Finally, we cannot end a chapter on the basic tools of analytical chemistry without mentioning the laboratory notebook. Your laboratory notebook is your most important tool when working in the lab, providing a complete record of all your work. If kept properly, you should be able to look back at your laboratory notebook several years from now and reconstruct the experiments on which you worked.

Your instructor will probably provide you with detailed instructions on how he or she wants you to maintain your notebook. Of course, you should expect to bring your notebook to the lab. Everything you do, measure, or observe while working in the lab should be recorded in your notebook as it takes place. Preparing data tables to organize your data will help ensure that you record the data you need and that you can find the data when it is time to calculate and analyze your results. Writing a narrative to accompany your data will help you remember what you did, why you did it, and why you thought it was significant. Reserve space for your calculations, for analyzing your data, and for interpreting your results. Take your notebook with you when you do research in the library.

Maintaining a laboratory notebook may seem like a great deal of effort, but if you do it well you have a permanent record of your work. Scientists working in academic, industrial, and governmental research labs rely on their notebooks to provide a written record of their work. Questions about research carried out at some time in the past can be answered by finding the appropriate pages in the laboratory notebook. A laboratory notebook is also a legal document that helps establish patent rights and proof of discovery.

3 2G KEY TERMS

balance (p. 25) concentration (p. 15) desiccant (p. 29) desiccator (p. 29) dilution (p. 31)
equivalent (p. 17)
equivalent weight (p. 17)
formality (p. 15)

formula weight (p. 17) meniscus (p. 29) molality (p. 18) molarity (p. 15)

| normality (p. 16) |
|---------------------------|
| parts per billion (p. 18) |
| parts per million (p. 18) |
| p-function (p. 19) |
| pipet (p. 27) |

```
quantitative transfer (p. 30)
scientific notation (p. 12)
significant figures (p. 13)
SI units (p. 12)
stock solution (p. 30)
```

volume percent (p. 18) volumetric flask (p. 26) weight percent (p. 18) weight-to-volume percent (p. 18)



2H SUMMARY

There are a few basic numerical and experimental tools with which you must be familiar. Fundamental measurements in analytical chemistry, such as mass and volume, use base SI units, such as the kilogram (kg) and the liter (L). Other units, such as power, are defined in terms of these base units. When reporting measurements, we must be careful to include only those digits that are significant and to maintain the uncertainty implied by these significant figures when transforming measurements into results.

The relative amount of a constituent in a sample is expressed as its concentration. There are many ways to express concentration, the most common of which are molarity, weight percent, volume percent, weight-to-volume percent, parts per million, and parts per billion. Concentrations also can be expressed using p-functions.

Stoichiometric relationships and calculations are important in many quantitative analyses. The stoichiometry between the reactants and products of a chemical reaction is given by the coefficients of a balanced chemical reaction. When it is inconvenient to balance reactions, conservation principles can be used to establish the stoichiometric relationships.

Balances, volumetric flasks, pipets, and ovens are standard pieces of laboratory instrumentation and equipment that are routinely used in almost all analytical work. You should be familiar with the proper use of this equipment. You also should be familiar with how to prepare a stock solution of known concentration, and how to prepare a dilute solution from a stock solution.

30

21 PROBLEMS

- Indicate how many significant figures are in each of the following numbers.
 - a. 903d. 0.0903
- b. 0.903 e. 0.09030
- c. 1.0903f. 9.03×10^2
- 2. Round each of the following to three significant figures.
 - a. 0.89377
- b. 0.89328
- c. 0.89350

- d. 0.8997
- e. 0.08907
- **3.** Round each of the following to the stated number of significant figures.
 - a. The atomic weight of carbon to four significant figures
 - b. The atomic weight of oxygen to three significant figures
 - c. Avogadro's number to four significant figures
 - d. Faraday's constant to three significant figures
- **4.** Report results for the following calculations to the correct number of significant figures.
 - a. 4.591 + 0.2309 + 67.1 =
 - b. 313 273.15 =
 - c. $712 \times 8.6 =$
 - d. 1.43/0.026 =
 - e. $(8.314 \times 298)/96485 =$
 - f. $\log(6.53 \times 10^{-5}) =$
 - g. $10^{-7.14}$ =
 - h. $(6.51 \times 10^{-5}) (8.14 \times 10^{-9}) =$
- **5.** A 12.1374-g sample of an ore containing Ni and Co was carried through Fresenius' analytical scheme shown in Figure 1.1. At point A the combined mass of Ni and Co was found to

- be 0.2306 g, and at point B the mass of Co was found to be 0.0813 g. Report the weight percent Ni in the ore to the correct number of significant figures.
- **6.** Hillebrand and Lundell's analytical scheme (see Figure 1.2) for the analysis of Ni in ores involves precipitating Ni²⁺ using dimethylgloxime. The formula for the precipitate is Ni(C₄H₇N₂O₂)₂. Calculate the precipitate's formula weight to the correct number of significant figures.
- **7.** An analyst wishes to add 256 mg of Cl^- to a reaction mixture. How many milliliters of 0.217 M BaCl₂ should be added?
- **8.** A solution of 0.10 M SO_4^{2-} is available. What is the normality of this solution when used in the following reactions?
 - a. $Pb^{2+}(aq) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s)$
 - b. $HCl(aq) + SO_4^{2-}(aq) \implies HSO_4^{-}(aq) + Cl^{-}(aq)$
 - c. $SO_4^{2-} + 4H_3O^+(aq) + 2e^- \implies H_2SO_3(aq) + 5H_2O(\ell)$
- **9.** The concentration of lead in an industrial waste stream is 0.28 ppm. What is its molar concentration?
- **10.** Commercially available concentrated hydrochloric acid is 37.0% w/w HCl. Its density is 1.18 g/mL. Using this information calculate (a) the molarity of concentrated HCl, and (b) the mass and volume (in milliliters) of solution containing 0.315 mol of HCl.
- **11.** The density of concentrated ammonia, which is 28.0% w/w NH₃, is 0.899 g/mL. What volume of this reagent should be diluted to 1.0×10^3 mL to make a solution that is 0.036 M in NH₃?

- **12.** A 250.0-mL aqueous solution contains 45.1 μg of a pesticide. Express the pesticide's concentration in weight percent, parts per million, and parts per billion.
- **13.** A city's water supply is fluoridated by adding NaF. The desired concentration of F⁻ is 1.6 ppm. How many milligrams of NaF should be added per gallon of treated water if the water supply already is 0.2 ppm in F⁻?
- **14.** What is the pH of a solution for which the concentration of H^+ is 6.92×10^{-6} M? What is the [H+] in a solution whose pH is 8.923?
- **15.** Using conservation principles, write stoichiometric relationships for the following
 - a. The precipitation of Mg²⁺ as Mg₂P₂O₇
 - The acid-base reaction between CaCO₃ and HCl in which H₂CO₃ is formed
 - c. The reaction between AgCl and NH₃ to form Ag(NH₃)₂⁺
 - d. The redox reaction between $Cr_2O_7^{2-}$ and Fe^{2+} to form Cr^{3+} and Fe^{3+}
- **16.** Calculate the molarity of a potassium dichromate solution prepared by placing 9.67 g of K₂Cr₂O₇ in a 100-mL volumetric flask, dissolving, and diluting to the calibration mark.
- **17.** For each of the following, explain how you would prepare 1.0 L of a solution that is 0.10 M in K⁺. Repeat for concentrations of 1.0×10^2 ppm K⁺ and 1.0% w/v K⁺.
 - a. KCl
- b. K₂SO₄
- c. K₃Fe(CN)₆

- **18.** A series of dilute NaCl solutions is prepared, starting with an initial stock solution of 0.100 M NaCl. Solution A is prepared by pipeting 10 mL of the stock solution into a 250-mL volumetric flask and diluting to volume. Solution B is prepared by pipeting 25 mL of solution A into a 100-mL volumetric flask and diluting to volume. Solution C is prepared by pipeting 20 mL of solution B into a 500-mL volumetric flask and diluting to volume. What is the molar concentration of NaCl in solutions A, B, and C?
- **19.** Calculate the molar concentration of NaCl, to the correct number of significant figures, if 1.917 g of NaCl is placed in a beaker and dissolved in 50 mL of water measured with a graduated cylinder. This solution is quantitatively transferred to a 250-mL volumetric flask and diluted to volume. Calculate the concentration of this second solution to the correct number of significant figures.
- **20.** What is the molar concentration of NO₃⁻ in a solution prepared by mixing 50.0 mL of 0.050 M KNO₃ with 40.0 mL of 0.075 M NaNO₃? What is pNO₃ for the mixture?
- **21.** What is the molar concentration of Cl⁻ in a solution prepared by mixing 25.0 mL of 0.025 M NaCl with 35.0 mL of 0.050 M BaCl₂? What is pCl for the mixture?
- **22.** To determine the concentration of ethanol in cognac a 5.00-mL sample of cognac is diluted to 0.500 L. Analysis of the diluted cognac gives an ethanol concentration of 0.0844 M. What is the molar concentration of ethanol in the undiluted cognac?

2 SUGGESTED READINGS

Two useful articles providing additional information on topics covered in this chapter are

MacCarthy, P. "A Novel Classification of Concentration Units," *J. Chem. Educ.* **1983**, *60*, 187–189.

Schwartz, L. M. "Propagation of Significant Figures," *J. Chem. Educ.* **1985**, *62*, 693–697.

A useful resource for information on maintaining a useful laboratory notebook is

Kanare, H. M. Writing the Laboratory Notebook, American Chemical Society: Washington, DC; 1985.



2K REFERENCES

 American Public Health Association. Standard Methods for the Analysis of Waters and Wastewaters, 19th ed., Washington, DC. 1995.

EXHIBIT F

2005

USP 28

THE UNITED STATES PHARMACOPEIA

NF 23

THE NATIONAL FORMULARY

By authority of the United States Pharmacopeial Convention, Inc., meeting at Washington, D.C., April 12–16, 2000. Prepared by the Council of Experts and published by the Board of Trustees

Official from January 1, 2005

The designation on the cover of this publication, "USP NF 2005," is for ease of identification only: The publication contains two separate compendia: The United States Pharmacopeia, Twenty-Eighth Revision, and the National Formulary, Twenty-Third Edition.

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represent and because of their heterogeneous composition. Ophthalmic solutions should be essentially free from particles that can be observed on visual inspection. The tests described herein are physical tests performed for the purpose of enumerating extraneous particles within specific size ranges.

Every ophthalmic solution for which the monograph includes a test for *Particulate matter* is subject to the particulate matter limits set forth for the test being applied, unless otherwise specified in the individual monograph. When higher limits are appropriate, they will be specified in the individual monograph. Ophthalmic preparations that are suspensions, emulsions, or gels are exempt from these requirements, as are medical devices. Refer to the specific monograph

when a question of test applicability occurs.

Light obscuration and microscopic procedures for the determination of particulate matter in ophthalmic solutions are identical to those for injections; therefore, where appropriate, Particulate Matter in Injections (788) is cross-referenced. This chapter procedes a test approach in two stages. The production is first tested by the light obscuration procedure (stage 1) of it fails to meet the prescribed limits, it must pass the national reasons the ophthalmic solution cannot be tested by light obscuration, microscopic testing may be used exclusively. Documentation is required, demonstrating that the light obscuration procedure is incapable of testing the ophthalmic solution or that it produces invalid results.

It is expected that most articles will meet the requirements on the basis of the light obscuration test alone; however, it may be necessary to test some articles by the light obscuration test followed by the microscopic test to reach a conclusion on conformance to requirements. Any product that is not a pure solution having a clarity and a viscosity approximating those of water may provide erroneous data when analyzed by the light obscuration counting method. Such materials may be analyzed by the microscopic counting method. In some instances, the viscosity of a material to be tested may be sufficiently high so as to preclude its analysis by either test method. In this event, a quantitative dilution with an appropriate dilution may be made to decrease viscosity, as necessary, to allow the analysis to be performed.

In the tests described below, the results obtained by examining a discrete unit or group of units for particulate matter cannot be extrapolated with certainty to other units that remain untested. Thus, sampling plans based on known operational factors must be developed if valid inferences are to be drawn from observed data to characterize the level of particulate matter in a large group of units. Sampling plans need to be based on consideration of product volume, particle numbers historically found to be present in comparison to limits, particle size distribution of particles present, and variability of

particle counts between units.

LIGHT OBSCURATION PARTICLE COUNT TEST

This test applies to ophthalmic solutions, including solutions constituted from sterile solids, for which a test for *Particulate matter* is specified in the individual monograph. The test counts suspended particles that are solid or liquid.

Test Apparatus, Instrument Standardization, Test Environment, Test Procedure, and Calculations—Proceed as directed for Light Obscuration Particle Count Test under Particulate Matter in Injections (788).

Interpretation—The ophthalmic solution meets the requirements of the test if the average number of particles present in the units tested does not exceed the appropriate value listed in Table 1. If the average number of particles exceeds the limit, test the article by the Microscopic Particle Count Test.

Table 1. Light Obscuration Test Particle Count

| | Diameter | | | |
|---------------------|-----------|----------|--|--|
| | ≥ 10 µm | ≥ 25 µm | | |
| Number of particles | 50 per mL | 5 per mL | | |

MICROSCOPIC PARTICLE COUNT TEST

Some articles cannot be tested meaningfully by light obscuration. In such cases, individual monographs clearly specify that only a microscopic particle count is to be performed. The microscopic particle count test enumerates subvisible, essentially solid, particulate matter in ophthalmic solutions, after collection on a microporous membrane filter. Some ophthalmic solutions, such as solutions that do not filter readily because of their high viscosity, may be exempted from analysis using the microscopic test.

When performing the microscopic test, do not attempt to size or enumerate amorphous, semiliquid, or otherwise morphologically indistinct materials that have the appearance of a stain or discoloration on the membrane surface. These materials show little or no surface relief and present a gelatinous or film-like appearance. Because in solution this material consists of units on the order of 1 µm or less, which may be counted only after aggregation or deformation on an analytical membrane, interpretation of enumeration may be aided by testing a sample of the solution by the light obscuration particle count method.

Test Apparatus, Test Environment, Test Procedure, and Enumeration of Particles—Proceed as directed for Microscopic Particle Count Test under Particulate Matter in Injections (788).

Interpretation—The ophthalmic solution meets the requirements of the test if the average number of particles present in the units tested does not exceed the appropriate value listed in *Table 2*.

Table 2. Microscopic Method Particle Count

| | Diameter | | | | | | |
|---------------------|-----------|-----------|----------|--|--|--|--|
| -1- | ≥ 10 µm | · ≥ 25 µm | ≥ 50 µm | | | | |
| Number of particles | 50 per mL | 5 per mL | 2 per mL | | | | |

(791) pH

For compendial purposes, pH is defined as the value given by a suitable, properly standardized, potentiometric instrument (pH meter) capable of reproducing pH values to 0.02 pH unit using an indicator electrode sensitive to hydrogen-ion activity, the glass electrode, and a suitable reference electrode. The instrument should be capable of sensing the potential across the electrode pair and, for pH standardization purposes, applying an adjustable potential to the circuit by manipulation of "standardization," "zero," "asymmetry," or "calibration" control, and should be able to control the change in millivolts per unit change in pH reading through a "temperature" and/or "slope" control. Measurements are made at 25 ± 2°, unless otherwise specified in the individual monograph or herein.

The pH scale is defined by the equation:

$$pH = pHs + (E - E_s)/k,$$

in which E and E_S are the measured potentials where the galvanic cell contains the solution under test, represented by pH, and the appropriate Buffer Solution for Standardization, represented by pHs, respectively. The value of k is the change in potential per unit change in pH and is theoretically $[0.05916 + 0.000198(t - 25^{\circ})]$ volts at any temperature t.

It should be emphasized that the definitions of pH, the pH scale, and the values assigned to the Buffer Solutions for Standardization are for the purpose of establishing a practical, operational system so that results may be compared between laboratories. The pH values thus measured do not correspond exactly to those obtained by the definition, pH = $-\log a_{t}$. So long as the solution being measured is sufficiently similar in composition to the buffer used for standardization, the operational pH corresponds fairly closely to the theoretical pH. Although no claim is made with respect to the suitability of the system for measuring hydrogen-ion activity or concentration, the values obtained are closely related to the activity of the hydrogen-ion in aqueous solutions.

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Where a pH meter is standardized by use of an aqueous buffer and then used to measure the "pH" of a nonaqueous solution or suspension, the ionization constant of the acid or base, the dielectric constant of the medium, the liquid-junction potential (which may give rise to errors of approximately 1 pH unit), and the hydrogen-ion response of the glass electrode are all changed. For these reasons, the values so obtained with solutions that are only partially aqueous in character can be regarded only as apparent pH values.

BUFFER SOLUTIONS FOR STANDARDIZATION OF THE pH METER

Buffer Solutions for Standardization are to be prepared as directed in the accompanying table.* Buffer salts of requisite purity can be obtained from the National Institute of Science and Technology. Solutions may be stored in hard glass or polyethylene bottles fitted with a tight closure or carbon dioxide-absorbing tube (soda lime). Fresh solutions should be prepared at intervals not to exceed 3 months using carbon dioxide-free water. The table indicates the pH of the buffer solutions as a function of temperature. The instructions presented here are for the preparation of solutions having the designated molal (m) concentrations. For convenience, and to facilitate their preparation, however, instructions are given in terms of dilution to a 1000-mL volume rather than specifying the use of 1000 g of solvent, which is the basis of the molality system of solution concentration. The indicated quantities cannot be computed simply without additional information.

Potassium Tetraoxalate, 0.05 m—Dissolve 12.61 g of $KH_3(C_2O_4)_2 \cdot 2H_2O$ in water to make 1000 mL.

Potassium Biphthalate, 0.05 m—Dissolve 10.12 g of KHC₈H₄O₄, previously dried at 110° for 1 hour, in water to make 1000 mL.

Equimolal Phosphate, 0.05 m—Dissolve 3.53 g of Na₂HPO₄ and 3.39 g of KH₂PO₄ each previously dried at 120° for 2 hours, in water to make 1000 mL.

Sodium Tetraborate, 0.01 m—Dissolve 3.80 g of Na₂B₄O₂ · 10H₂O in water to make 1000 mL. Protect from absorption of carbon dioxide.

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Calcium Hydroxide, saturated at 25°—Shake an excess of calcium hydroxide with water, and decant at 25° before use. Protect from absorption of carbon dioxide.

Because of variations in the nature and operation of the available pH meters, it is not practicable to give universally applicable directions for the potentiometric determinations of pH. The general principles to be followed in carrying out the instructions provided for each instrument by its manufacturer are set forth in the following paragraphs. Examine the electrodes and, if present, the salt bridge prior to use. If necessary, replenish the salt bridge solution, and observe other precautions indicated by the instrument or electrode manufacturer.

To standardize the pH meter, select two Buffer Solutions for Standardization whose difference in pH does not exceed 4 units and such that the expected pH of the material under test falls between them. Fill the cell with one of the Buffer Solutions for Standardization at the temperature at which the test material is to be measured. Set the "temperature" control at the temperature of the solution, and adjust the calibration control to make the observed pH value identical with that tabulated. Rinse the electrodes and cell with several portions of the second Buffer Solution for Standardization, then fill the cell with it, at the same temperature as the material to be measured. The pH of the second buffer solution is within ± 0.07 pH unit of the tabulated value. If a larger deviation is noted, examine the electrodes and, if they are faulty, replace them. Adjust the "slope" or "temperature" control to make the observed pH value identical with that tabulated. Repeat the standardization until both Buffer Solutions for Standardization give observed pH values within 0.02 pH unit of the tabulated value without further adjustment of the controls. When the system is functioning satisfactorily, rinse the electrodes and cell several times with a few portions of the test material, fill the cell with the test material, and read the pH value. Use carbon dioxide-free water (see Water in the section Reagents, Indicators, and Solutions) for solution or dilution of test material in pH determinations. In all pH measurements, allow a sufficient time for stabilization.

Where approximate pH values suffice, indicators and test papers (see Indicators and Indicator Test Papers, in the section Reagents, Indicators, and Solutions) may be suitable.

For a discussion of buffers, and for the composition of standard buffer solutions called for in compendial tests and assays, see Buffer Solutions in the section Reagents, Indicators, and Solutions.

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pH Values of Buffer Solutions for Standardization

| Tempera- ture, °C | Potassium Tetraoxalate, 0.05 m | Potassium Biphthalate, 0.05 m | Equimolal Phosphate, 0.05 m | Sodium Tetraborate, 0.01 m | Calcium Hydroxide, Saturated at 25° |
|----------------------|-----------------------------------|----------------------------------|--------------------------------|----------------------------|--|
| 10 | 1.67 | 4.00 | 6.92 | 9.33 | 13.00 |
| 15 | 1.67 | 4.00 | 6.90 | 9.28 | 12.81 |
| 20 | 1.68 | 4.00 | 6.88 | 9.23 | 12.63 |
| 25 | 1.68 | 4.01 | 6.86 | 9.18 | 12.45 |
| 30 | 1.68 | 4.02 | 6.85 | 9.14 | 12.29 |
| 35 | 1.69 | 4.02 | 6.84 | 9.10 | 12.13 141 |
| 40 | 1.69 | 4.04 | 6.84 | 9.07 | 11.98 |
| 45 | 1.70 | 4.05 | 6.83 | 9.04 | 11.84 |
| 50 | 1.71 | 4.06 | 6.83 | 9.01 | . 11.71 |
| 55 | 1.72 | 4.08 | 6.83 | 8.99 | 11.57 |
| 60 | 1.72 | 4.09 | 6.84 | 8.96 | 11.45 |

^{*}Commercially available buffer solutions for pH meter standardization, standardized by methods traceable to the National Institute of Standards and Technology (NIST), labeled with a pH value accurate to 0.01 pH unit may be used. For standardization solutions having a pH lower than 4, a labeled accuracy of 0.02 is acceptable. Solutions prepared from ACS reagent grade materials or other suitable materials, in the stated quantities, may be used provided the pH of the resultant solution is the same as that of the solution prepared from the NIST certified material.

EXHIBIT G

2006

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THE UNITED STATES PHARMACOPEIA

Contents

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NF 24

THE NATIONAL FORMULARY

By authority of The United States Pharmacopeial Convention, meeting at Washington, D.C., March 9–13, 2005. Prepared by the Council of Experts and published by the Board of Trustees

Official from January 1, 2006

The designation on the cover of this publication, "USP NF 2006," is for ease of identification only. The publication contains two separate compendia: *The United States Pharmacopeia*, Twenty-Ninth Revision, and the *National Formulary*, Twenty-Fourth Edition.

THE UNITED STATES PHARMACOPEIAL CONVENTION 12601 Twinbrook Parkway, Rockville, MD 20852

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Test Apparatus, Test Environment, Test Procedure, and Enumeration of Particles—Proceed as directed for Microscopic Particle Count Test under Particulate Matter in Injections (788).

Interpretation—The ophthalmic solution meets the requirements of the test if the average number of particles present in the units tested does not exceed the appropriate value listed in *Table 2*.

Table 2. Microscopic Method Particle Count

| | | Diameter | |
|---------------------|-----------|----------|----------|
| | ≥ 10 µm | ≥ 25 µm | ≥ 50 µm |
| Number of particles | 50 per mL | 5 per mL | 2 per mL |

(791)pH

For compendial purposes, pH is defined as the value given by a suitable, properly standardized, potentiometric instrument (pH meter) capable of reproducing pH values to 0.02 pH unit using an indicator electrode sensitive to hydrogen-ion activity, the glass electrode, and a suitable reference electrode. The instrument should be capable of sensing the potential across the electrode pair and, for pH standardization purposes, applying an adjustable potential to the circuit by manipulation of "standardization," "zero," "asymmetry," or "calibration" control, and should be able to control the change in millivolts per unit change in pH reading through a "temperature" and/or "slope" control. Measurements are made at $25\pm2^\circ$, unless otherwise specified in the individual monograph or herein.

The pH scale is defined by the equation:

$$pH = pHs + (E - E_s)/k,$$

in which E and E_s are the measured potentials where the galvanic cell contains the solution under test, represented by pH, and the appropriate Buffer Solution for Standardization, represented by pHs, respectively. The value of k is the change in potential per unit change in pH and is theoretically $[0.05916 + 0.000198(t-25^\circ)]$ volts at any temperature t.

It should be emphasized that the definitions of pH, the pH scale, and the values assigned to the Buffer Solutions for Standardization are for the purpose of establishing a practical, operational system so that results may be compared between laboratories. The pH values

thus measured do not correspond exactly to those obtained by the definition, $pH = -\log a_n^+$. So long as the solution being measured is sufficiently similar in composition to the buffer used for standardization, the operational pH corresponds fairly closely to the theoretical pH. Although no claim is made with respect to the suitability of the system for measuring hydrogen-ion activity or concentration, the values obtained are closely related to the activity of the hydrogen-ion in aqueous solutions.

Where a pH meter is standardized by use of an aqueous buffer and then used to measure the "pH" of a nonaqueous solution or suspension, the ionization constant of the acid or base, the dielectric constant of the medium, the liquid-junction potential (which may give rise to errors of approximately 1 pH unit), and the hydrogen-ion response of the glass electrode are all changed. For these reasons, the values so obtained with solutions that are only partially aqueous in character can be regarded only as apparent pH values.

BUFFER SOLUTIONS FOR STANDARDIZATION OF THE PH METER

Buffer Solutions for Standardization are to be prepared as directed in the accompanying table. Buffer salts of requisite purity can be obtained from the National Institute of Science and Technology. Solutions may be stored in hard glass or polyethylene bottles fitted with a tight elosure or carbon dioxide-absorbing tube (soda lime). Fresh solutions should be prepared at intervals not to exceed 3 months using carbon dioxide-free water. The table indicates the pH of the buffer solutions as a function of temperature. The instructions presented here are for the preparation of solutions having the designated molal (m) concentrations. For convenience, and to facilitate their preparation, however, instructions are given in terms of dilution to a 1000-mL volume rather than specifying the use of 1000 g of solvent, which is the basis of the molality system of solution concentration. The indicated quantities cannot be computed simply without additional information.

Potassium Tetraoxalate, 0.05 m—Dissolve 12.61 g of KH₃(C₂O₄)₂ · 2H₂O in water to make 1000 mL.

Potassium Biphthalate, 0.05 m—Dissolve 10.12 g of KHC₈H₄O₄, previously dried at 110° for 1 hour, in water to make 1000 mL.

Equimolal Phosphate, 0.05 m—Dissolve 3.53 g of Na₂HPO₄ and 3.39 g of KH₂PO₄ each previously dried at 120° for 2 hours, in water to make 1000 mL.

Sodium Tetraborate, 0.01 m—Dissolve 3.80 g of Na₂B₄O₇ · 10H₂O in water to make 1000 mL. Protect from absorption of carbon dioxide.

Calcium Hydroxide, saturated at 25°—Shake an excess of calcium hydroxide with water, and decant at 25° before use. Protect from absorption of carbon dioxide.

pH Values of Buffer Solutions for Standardization

| Tempera- ture, °C | Potassium Tetraoxalate, 0.05 m | Potassium Biphthalate, 0.05 m | Equimolal Phosphate, So | dium Tetraborate, 0.01 m | Calcium Hydroxide, Saturated at 25 |
|----------------------|-----------------------------------|----------------------------------|-------------------------|-----------------------------|---------------------------------------|
| 10 | 1.67 | 4.00 | 6.92 | 9.33 | 13.00 |
| 15 | 1.67 | 4.00 | 6.90 | 9.28 | 12.81 |
| 20 | 1.68 | 4.00 | 6.88 | 9.23 | 12.63 |
| 25 | 1.68 | 4.01 | 6.86 | 9.18 | 12.45 |
| 30 | 1.68 | 4.02 | 6.85 | 9.14 | 12.29 |
| 35 | 1.69 | 4.02 | 6.84 | 9.10 | 12.13 |
| 40 | 1.69 | 4.04 | 6.84 | 9.07 | 11.98 |
| 45 | 1.70 | 4.05 | 6.83 | 9.04 | 11.84 |
| 50 | 1.71 | 4.06 | 6.83 | 9.01 | 11.71 |
| 55 | 1.72 | 4.08 | 6.83 | 8.99 | 11.57 |
| 60 | 1.72 | 4.09 | 6.84 | 8.96 | 11.45 |

^{*}Commercially available buffer solutions for pH meter standardization, standardized by methods traceable to the National Institute of Standards and Technology (NIST), labeled with a pH value accurate to 0.01 pH unit may be used. For standardization solutions having a pH lower than 4, a labeled accuracy of 0.02 is acceptable. Solutions prepared from ACS reagent grade materials or other suitable materials, in the stated quantities, may be used provided the pH of the resultant solution is the same as that of the solution prepared from the NIST cattifed material. EPO 000113

Because of variations in the nature and operation of the available pH meters, it is not practicable to give universally applicable directions for the potentiometric determinations of pH. The general principles to be followed in carrying out the instructions provided for each instrument by its manufacturer are set forth in the following paragraphs. Examine the electrodes and, if present, the salt bridge prior to use. If necessary, replenish the salt bridge solution, and observe other precautions indicated by the instrument or electrode

To standardize the pH meter, select two Buffer Solutions for Standardization whose difference in pH does not exceed 4 units and such that the expected pH of the material under test falls between them. Fill the cell with one of the Buffer Solutions for Standardization at the temperature at which the test material is to be measured. Set the 'temperature" control at the temperature of the solution, and adjust the calibration control to make the observed pH value identical with that tabulated. Rinse the electrodes and cell with several portions of the second Buffer Solution for Standardization, then fill the cell with it, at the same temperature as the material to be measured. The pH of the second buffer solution is within ±0.07 pH unit of the tabulated value. If a larger deviation is noted, examine the electrodes and, if they are faulty, replace them. Adjust the "slope" or "temperature" control to make the observed pH value identical with that tabulated. Repeat the standardization until both Buffer Solutions for Standardization give observed pH values within 0.02 pH unit of the tabulated value without further adjustment of the controls. When the system is functioning satisfactorily, rinse the electrodes and cell several times with a few portions of the test material, fill the cell with the test material, and read the pH value. Use carbon dioxide-free water (see Water in the section Reagents, Indicators, and Solutions) for solution or dilution of test material in pH determinations. In all pH measurements, allow a sufficient time for stabilization.

Where approximate pH values suffice, indicators and test papers (see Indicators and Indicator Test Papers, in the section Reagents,

Indicators, and Solutions) may be suitable.

For a discussion of buffers, and for the composition of standard buffer solutions called for in compendial tests and assays, see Buffer Solutions in the section Reagents, Indicators, and Solutions.

(795) PHARMACEUTICAL COMPOUNDING—NONSTERILE PREPARATIONS

For the purposes of this chapter, the pharmacist or other licensed health care professional responsible for preparing the compounded

preparations is referred to as "compounder"

Compounding is an integral part of pharmacy practice and is essential to the provision of health care. The purpose of this chapter and applicable monographs on formulation is to help define what constitutes good compounding practices and to provide general information to enhance the compounder's ability in the compounding facility to extemporaneously compound preparations that are of acceptable strength, quality, and purity.

Compounding is different from manufacturing, which is guided by GMPs (see Good Manufacturing Practices for Bulk Pharmaceutical Excipients (1078)). Some of the characteristics or criteria that differentiate compounding from manufacturing include the existence of specific practitioner-patient-compounder relationships; the quantity of medication prepared in anticipation of receiving a prescription or a prescription order; and the conditions of sale, which are limited to

specific prescription orders.

The pharmacist's responsibilities in compounding drug preparations are to dispense the finished preparation in accordance with a prescription or a prescriber's order or intent and to dispense those preparations in compliance with the requirements established by the Boards of Pharmacy and other regulatory agencies. Compounders must be familiar with statutes and regulations that govern compounding because these requirements vary from state to state.

The compounder is responsible for compounding preparations of acceptable strength, quality, and purity with appropriate packaging and labeling in accordance with good compounding practices (see $Good\ Compounding\ Practices\ \langle 1075\rangle$), official standards, and relevant scientific data and information. Compounders engaging in

compounding should have to continually expand their compounding knowledge by participating in seminars, studying appropriate literature, and consulting colleagues.

RESPONSIBILITY OF THE COMPOUNDER

The compounder is responsible for ensuring that the quality is built into the compounded preparations of products, with key factors including at least the following general principles. (See also Good Compounding Practices (1075).)

(1) Personnel are capable and qualified to perform their assigned

Ingredients used in compounding have their expected identity,

quality, and purity.

Compounded preparations are of acceptable strength, quality, and purity, with appropriate packaging and labeling, and prepared in accordance with good compounding practices, official standards, and relevant scientific data and information.

Critical processes are validated to ensure that procedures, when used, will consistently result in the expected qualities in the

finished preparation.

The compounding environment is suitable for its intended

purpose.

- Appropriate stability evaluation is performed or determined from the literature for establishing reliable beyond-use dating to ensure that the finished preparations have their expected potency, purity, quality, and characteristics, at least until the labeled beyond-use date.
- There is assurance that processes are always carried out as intended or specified and are under control.
- Compounding conditions and procedures are adequate for

preventing errors.

Adequate procedures and records exist for investigating and correcting failures or problems in compounding, testing, or in the preparation itself.

COMPOUNDING ENVIRONMENT

Facilities

Areas designated for compounding have adequate space for the orderly placement of equipment and materials to prevent mixups between ingredients, containers, labels, in-process materials, and finished preparations. The compounding area is also to be designed, arranged, used, and maintained to prevent adventitious crosscontamination. Areas used for sterile preparations are to be separated and distinct from the nonsterile compounding area (see Environmental Quality and Control under Pharmaceutical Compounding— Sterile Preparations (797)). The entire compounding area is to be well-lighted. Heating, ventilation, and air conditioning systems are to be controlled to avoid decomposition of chemicals (see Storage Temperature under Preservation, Packaging, Storage, and Labeling in the General Notices and Requirements and the manufacturers labeled storage conditions). Storage areas provide an environment suitably controlled to ensure quality and stability of bulk chemicals and finished preparations.

Potable water is to be supplied for hand and equipment washing. This water meets the standards prescribed in the EPA's National Primary Drinking Water Regulations (40 CFR Part 141). Purified Water must be used for compounding nonsterile drug preparations when formulations indicate the inclusion of water. Purified Water must also be used for rinsing equipment and utensils. In those cases when a water is used to prepare a sterile preparation, Water for Injection, Sterile Water for Injection, or Bacteriostatic Water for Injection must be used (see Water for Pharmaceutical Purposes (1231) and Pharmaceutical Compounding-Sterile Preparations

Compounding areas are to be maintained in a clean and sanitary condition. Adequate washing facilities are to be provided, including hot and cold water, soap or detergent, and air driers or single-service towels. Sewage, trash, and other refuse in the compounding area is to be disposed of in a safe, sanitary, and timely manner. Equipment is to be thoroughly cleaned promptly after use to avoid cross-contamination of ingredients and preparations. Special precautions are to be MYLAN_EPO_000114

EXHIBIT H

THE UNITED STATES PHARMACOPEIA

THE NATIONAL FORMULARY

By authority of the United States Pharmacopeial Convention, Inc., meeting at Washington, D.C., March 8-10, 1990. Prepared by the Committee of Revision and published by the Board of Trustees

Official from January 1, 1995



UNITED STATES PHARMACOPEIAL CONVENTION, INC. 12601 Twinbrook Parkway, Rockville, MD 20852

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UNITED STATES PHARMACOPEIAL CONVENTION, INC. 12601 Twinbrook Parkway, Rockville, MD 20852

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THE UNITED STATES PHARMACOPEIA

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By authority of the United States Pharmacopeial Convention, Inc., meeting at Washington, D.C., March 8-10, 1990. Prepared by the Committee of Revision and published by the Board of Trustees

Official from January 1, 1995



UNITED STATES PHARMACOPEIAL CONVENTION, INC. 12601 Twinbrook Parkway, Rockville, MD 20852

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All rights reserved ISSN 0195-7996 ISBN 0-913595-76-4 (cloth) 0-913595-81-0 (leather)

Printed by Rand McNally, 1133 County Street, Taunton, MA 02780-3795

To perform a partial count of the particles on a membrane, start at the right center edge of the filtration area and begin counting adjacent GFOVs. When the left edge of the filtration area is reached, move one GFOV toward the top of the filter and continue counting GFOVs by moving in the opposite direction. Moving from one GFOV to the next can be accomplished by one of two methods. One method is to define a landmark (particle or surface irregularity in the filter) and move over one GFOV in relation to the landmark. A second method is to use the vernier on the microscope stage to move one millimeter between GFOVs. To facilitate the latter, adjust the microscope x and y stage positioning controls to a whole number at the starting position at the center right edge of the filtration area, then each GFOV will be one whole division of movement of the x stage positioning control. If the top of the filtration area is reached before the desired number of GFOVs is reached, begin again at the right center edge of the filtration area one GFOV lower than the first time. This time move downward on the membrane when the end of a row of GFOVs is reached. Continue as before until the number of GFOVs is complete.

For large-volume injections, if a partial count procedure for the ≥ 10 - μ m and ≥ 25 - μ m size ranges is used, calculate the particles per mL by the formula:

$PA_{t}/A_{p}V$

in which P is the number of particles counted, A_t is the filtration area, in mm², of the membrane, A_p is the partial area counted, in mm², based on the number of graticule fields counted, a V is the volume, in mL, of solution filtered. For a solution pool (for small-volume injection units containing less than 25 mL) or for a single unit of a small-volume injection, calculate the number of particles per unit by the formula:

$PA_{t}/A_{p}n$

in which n is the number of units counted (1 in the case of a single unit), and the other terms are as defined above.

Interpretation

The injection meets the requirements of the test if the average number of particles present in the units tested does not exceed the values listed in Table 2.

Table 2. Microscopic Method Particle Count.

| | ≥10 μm | ≥25 μm |
|-----------------------------|--------|----------|
| Large-volume Injections: | 12 | 2 per mL |

(791) pH

For compendial purposes, pH is defined as the value given by a suitable, properly standardized, potentiometric instrument (pH meter) capable of reproducing pH values to 0.02 pH unit using an indicator electrode sensitive to hydrogen-ion activity, the glass electrode, and a suitable reference electrode such as calomel or silver-silver chloride. The instrument should be capable of sensing the potential across the electrode pair and, for pH standardization purposes, applying an adjustable potential to the circuit by manipulation of "standardization," "zero," "asymmetry," or "calibration" control, and should be able to control the change in millivolts per unit change in pH reading through a "temperature" and/or "slope" control. Measurements are made at 25 \pm 2°, unless otherwise specified in the individual monograph or herein.

The pH scale is defined by the equation:

$$pH = pHs + (E - E_S)/k$$

in which E and $E_{\rm S}$ are the measured potentials where the galvanic cell contains the solution under test, represented by pH, and the appropriate Buffer Solution for Standardization, represented by pHs, respectively. The value of k is the change in potential per unit change in pH and is theoretically $[0.05916 + 0.000198(t - 25^{\circ})]$ volts at any temperature t. This operational pH scale

is established by assigning rounded pH values to the Buffer Solutions for Standardization from the corresponding National Institute of Standards and Technology molal solutions.

It should be emphasized that the definitions of pH, the pH scale, and the values assigned to the Buffer Solutions for Standardization are for the purpose of establishing a practical, operational system so that results may be compared between laboratories. The pH values thus measured do not correspond exactly to those obtained by the classical definition, $pH = -\log [H^+(aq)]$. So long as the solution being measured is sufficiently similar in composition to the buffer used for standardization, the operational pH corresponds fairly closely to the theoretical pH. Although no claim is made with respect to the suitability of the system for measuring hydrogen-ion activity or concentration, the values obtained are closely related to the activity of the hydrogen ion in aqueous solutions.

Where a pH meter is standardized by use of an aqueous buffer and then used to measure the "pH" of a nonaqueous solution or suspension, the ionization constant of the acid or base, the dielectric constant of the medium, the liquid-junction potential (which may give rise to errors of approximately 1 pH unit), and the hydrogen-ion response of the glass electrode are all changed. For these reasons, the values so obtained with solutions that are only partially aqueous in character can be regarded only as apparent pH values. However, acidity may be accurately measured with the proper use of electrodes and instrument standardization.

Buffer Solutions for Standardization of the pH Meter-

Buffer Solutions for Standardization are to be prepared as directed in the accompanying table. Buffer salts of requisite purity can be obtained from the National Institute of Science and Technology. Solutions may be stored in chemically resistant, tight containers, such as Type I glass bottles. Fresh solutions should be prepared at intervals not to exceed 3 months. The table indicates the pH of the buffer solutions as a function of temperature. The instructions presented here are for the preparation of solutions having the designated molal (m) concentrations. For convenience, and to facilitate their preparation, however, instructions are given in terms of dilution to a 1000-mL volume rather than specifying the use of 1000 g of solvent, which is the basis of the molality system of solution concentration. The indicated quantities cannot be computed simply without additional information.

Potassium Tetraoxalate, 0.05 m—Dissolve 12.61 g of KH₃(C₂O₄)₂·2H₂O in water to make 1000 mL.

Potassium Biphthalate, 0.05 m—Dissolve 10.12 g of $KHC_8H_4O_4$, previously dried at 110° for 1 hour, in water to make 1000 mL.

Equimolal Phosphate, 0.05 m—Dissolve 3.53 g of Na₂HPO₄ and 3.39 g of KH₂PO₄, each previously dried at 120° for 2 hours, in water to make 1000 mL.

Sodium Tetraborate, 0.01 m—Dissolve 3.80 g of Na₂B₄O₇·-10H₂O in water to make 1000 mL. Protect from absorption of carbon dioxide.

Calcium Hydroxide, saturated at 25°—Shake an excess of calcium hydroxide with water, and decant at 25° before use. Protect from absorption of carbon dioxide.

Because of variations in the nature and operation of the available pH meters, it is not practicable to give universally applicable directions for the potentiometric determinations of pH. The general principles to be followed in carrying out the instructions provided for each instrument by its manufacturer are set forth in the following paragraphs. Examine the electrodes and, if present, the salt bridge prior to use. If necessary, replenish the salt bridge solution, and observe other precautions indicated by the instrument or electrode manufacturer.

To standardize the pH meter, select two Buffer Solutions for Standardization whose difference in pH does not exceed 4 units

^{*} Commercially available buffer solutions for pH meter standardization, standardized by methods traceable to the National Institute of Standards and Technology (NIST), labeled with a pH value accurate to 0.01 pH unit, and provided with a table showing the pH values at various temperatures, may be used. Solutions prepared from ACS reagent grade materials or other suitable materials, in the stated quantities, may be used provided the pH of the resultant solution is the same as that of the solution prepared from the NIST certified material.

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pH Values of Buffer Solutions for Standardization

| m | Temperat | ure, | Potassi Tetraoxa | late, | Potassium Biphthalate, Q.05 m | Equimolal Phosphate, 0.05 m | | Sodium Tetraborate, 0.01 m | Calcium Hydroxide, Saturated at 25° |
|----|-----------------|---------|----------------------|-------|-------------------------------------|-----------------------------|-----|----------------------------------|---|
| Ĵ, | 10 15 20 | , roi , | 1.67 1.67 1.68 | บ่า | 3 4(00 - 3) 4.00 - 3 4.00 | 6.92 | 3 | 9.33 9.28 9.23 | 13.00 12.81 12.63 |
| | 25 30 35 | - 100 | 1.68 1.68 1.69 | | 4.01 4.02 4.02 | 6.86 6.85 6.84 | | 9.18 9.14 9.10 | 12.45 12.29 12.13 |
| ř | 40 45 | | 1:69 1.70 | | 4.04 4.05 | 6.84 6.83 | - ` | 9.07 9.04 | 11.98 11.84 |
| | 50. 55 60 | t re | 1.71 1.72 1.72 | | 4.06 4.08 4.09 | 6.83 6.83 6.84 | | 9.01 8.99 8.96 | 11.71 11.57 11.45 |

and such that the expected pH of the material under test falls between them. Fill the cell with one of the Buffer Solutions for Standardization at the temperature at which the test material is to be measured. Set the "temperature" control at the temperature of the solution, and adjust the calibration control to make the observed pH value identical with that tabulated. Rinse the electrodes and cell with several portions of the second Buffer Solution for Standardization, then fill the cell with it, at the same temperature as the material to be measured. The pH of the second buffer solution is within ±0.07 pH unit of the tabulated value. If a larger deviation is noted, examine the electrodes and, if they are faulty, replace them. Adjust the "slope" or "temperature" control to make the observed pH value identical with that tabulated. Repeat the standardization until both Buffer Solutions for Standardization give observed pH values within 0.02 pH unit of the tabulated value without further adjustment of the controls. When the system is functioning satisfactorily, rinse the electrodes and cell several times with a few portions of the test material, fill the cell with the test material, and read the pH value. Use carbon dioxide-free water (see Water in the section Reagents, Indicators, and Solutions) for solution or dilution of test material in pH determinations.

Where approximate pH values suffice, indicators and test papers (see *Indicators and Indicator Test Papers*, in the section Reagents, Indicators, and Solutions) may be suitable.

For a discussion of buffers, and for the composition of standard buffer solutions called for in compendial tests and assays, see Buffer Solutions in the section Reagents, Indicators, and Solutions.

(801) POLAROGRAPHY

Polarography is an electrochemical method of analysis based on the measurement of the current flow resulting from the electrolysis of a solution at a polarizable microelectrode, as a function of an applied voltage. The polarogram (see Figure 1) obtained by this measurement provides qualitative and quantitative information on electro-reducible and electro-oxidizable substances. The normal concentration range for substances being analyzed is from 10^{-2} molar to 10^{-5} molar.

In direct current (dc) polarography, the microelectrode is a dropping mercury electrode (DME) consisting of small reproducible drops of mercury flowing from the orifice of a capillary tube connected to a mercury reservoir. A saturated calomel electrode (SCE) with a large surface area is the most commonly employed reference electrode. As the voltage applied to the cell increases, only a very small residual current flows until the substance under assay undergoes reduction or oxidation. Then the current increases, at first gradually, then almost linearly with voltage, and it gradually reaches a limiting value as is shown in Figure 1. On the initial rising portion of the polarographic wave, the increased flow of current results in a decrease in the concentration of the electro-active species at the electrode surface. As the voltage and current increase, the concentration of the reactive species decreases further to a minimal value at the electrode surface. The current is then limited by the rate at which the reacting species can diffuse from the bulk of the solution to the surface of the microelectrode. The final current rise is caused by the reaction of the supporting electrolyte. This large concentration of electrolyte is inert within the potential range used in the analysis, and it prevents the reactive species from reaching the electrode by electrical migration, thus assuring that the limiting current is diffusion-controlled.

Since, in the case of the DME, the electrode surface is being constantly renewed in a cyclic fashion, the current increases from a small value as the drop begins to form to a maximum value as the drop falls. By the use of a suitable recorder to measure the current, the characteristic saw-toothed record is obtained. The limiting current is the sum of the residual and the diffusion currents. The residual current is subtracted from the limiting current to give the wave height.

Ilkovic Equation—The linear relationship between the diffusion current (i_d) and the concentration of electro-active species is shown by the Ilkovic equation:

$$i_d = 708nD^{1/2}Cm^{2/3}t^{1/6},$$

in which t_d is the maximum current in microamperes, n is the number of electrons required per molecule of electro-active substance, D is its diffusion coefficient, in square cm per second, C is the concentration, in millimoles per liter, m is the rate of mercury flow from the DME, in mg per second, and t is the drop time, in seconds.

Modern polarographs are equipped with recorders capable of following the current during the latter portion of the drop life;

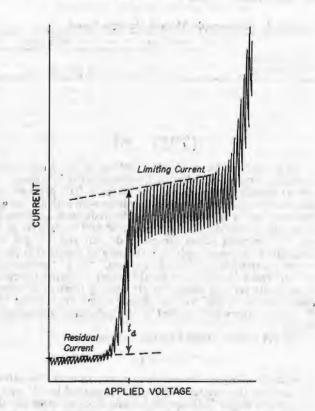


Fig. 1. Typical Polarogram Showing Change in Current Flow with Increasing Potential Applied to the Dropping Mercury Electrode.

MYLAN_EPO_000120

EXHIBIT I

The United States Pharmacopeia

TWENTY-FIRST REVISION

Official from January 1, 1985

The National Formulary

SIXTEENTH EDITION

Official from January 1, 1985

United States Pharmacopeial Convention, Inc. 12601 Twinbrook Parkway, Rockville, Md. 20852



United Sta

Pharmacopeia

WENTY-FIRST REVISION

© 1984 The United States Pharmacopeial Convention, Inc. 12601 Twinbrook Parkway, Rockville, Md. 20852 All rights reserved Glassware and Closure Cleaning Clean glassware and closures by immersing and scrubbing in warm, nonionic detergent solution, then rinse in flowing warm tap water, followed by rinsing in filtered water. Finally, pressure-rinse in filtered water, using a hand-held pressure nozzle with final filter.

Particulate Control Test—Conduct this test to determine that the environment is suitable for the analysis and that the glassware is properly cleaned, and to assure the water to be used for analysis is particle-free. Using filtered water and cleaned glassware, take 5 consecutive water samples of 5 mL each. Invert each sample 25 times. Degas by allowing to stand for 2 minutes. Stir each water sample at a speed sufficient to maintain a slight vortex throughout the analysis. If 5 particles of 25-µm or greater size are observed for the combined 25 mL, either the environment is not suitable for particulate analysis or the filtered water and glassware have not been properly prepared. Repeat the preparatory steps until environment, water, and glassware are suitable for this test.

Calibration—Calibrate the instrument with 3 standards consisting of monosized polystyrene spheres, approximately $10~\mu m$, 20 μm , and 30 μm , in an aqueous vehicle. Use freshly obtained particulate reference standards to reduce particle agglomeration and assure particle purity. Use the "moving window" variation of the delta half-count method. Analyze 4 consecutive, known volumes following proper cleansing procedures (see Test Preparation) and agitation of the standard. Discard data from first volume sampled. The average count of the remaining 3 volumes sampled is within $\pm 5\%$ of the stated number specified for each particle size range in the standard.

Test Preparation—Prepare the test specimens in the following sequence:

Remove outer closures, sealing bands, and any paper labels, wash the exterior of containers as described under *Glassware and Closure Cleaning*, and dry in a particle-free air flow.

Determination-

(A) Liquid Products of 5-mL or Greater Volume

(1) Mix by inverting 25 times within 10 seconds.

(2) Degas by ultrasonication for 30 seconds or by allowing to stand for 2 minutes.

(3) Open the container.

(4) Gently stir contents of containers by hand swirling or by mechanical means, taking care not to introduce air bubbles or contamination. Perform the sampling within 15 seconds, or stir throughout the analysis.

(5) Take 4 consecutive portions, each not less than 1 mL.

Discard the data from the first portion.

(6) Rinse sensor with filtered water after each container sampled.

NOTE—Set the container sampling unit to draw a minimum volume of product in excess of the sample volume, particularly when 5-mL vials are being sampled at 1-mL volumes.

(B) Dry or Lyophilized Products

- Open the container, taking care not to contaminate the opening or cover.
- (2) Constitute with required volume of filtered water, or with the appropriate filtered diluent if water is not suitable.
 - (3) Replace cover, and agitate as in (A).

(4) Analyze as in (A).

(C) Products of Less Than 5-mL Volume

Agitate as in (A).

(2) Open the container.

- (3) Remove contents, and place in a container having a capacity of 10 mL or more.
- (4) Add a sufficient volume of particle-free liquid for analysis, taking care to measure the volume of product and make up the liquid.
 - (5) Cover the container and analyze as in (A).

Calculations—Average the counts resulting from the 3 portions of the sample analyzed. Calculate the number of particles in each container, P_C , by multiplying the average count per portion, \overline{C} , times the volume, in mL, of each container, V_C , divided by the volume, in mL of each portion analyzed, V_P ; i.e., $P_C = \overline{C}V_C/V_P$.

Interpretation—The small-volume Injection meets the requirements of the test if it contains not more than 10,000 particles per container that are equal to or greater than 10 μ m in effective spherical diameter and/or 1000 particles per container equal to or greater than 25 μ m in effective spherical diameter.

(791) pH

For compendial purposes, pH is defined as the value given by a suitable, properly standardized, potentiometric instrument (pH meter) capable of reproducing pH values to 0.02 pH unit using an indicator electrode sensitive to hydrogen-ion activity, the glass electrode, and a suitable reference electrode such as calomel or silver-silver chloride. The instrument should be capable of sensing the potential across the electrode pair and, for pH standardization purposes, applying an adjustable potential to the circuit by manipulation of "standardization," "zero," "asymmetry," or "calibration" control, and should be able to control the change in millivolts per unit change in pH reading through a "temperature" and/or "slope" control. Measurements are made at $25 \pm 2^{\circ}$, unless otherwise specified in the individual monograph or herein.

The pH scale is defined by the equation $pH = pHs + (E - E_S)/k$, in which E and E_S are the measured potentials where the galvanic cell contains the solution under test, represented by pH, and the appropriate Buffer Solution for Standardization, represented by pHs, respectively. The value of k is the change in potential per unit change in pH and is theoretically $[0.05916 + 0.000198(t - 25^\circ)]$ volts at any temperature t. This operational pH scale is established by assigning rounded pH values to the Buffer Solutions for Standardization from the corresponding National Bureau of Standards modal solutions.

It should be emphasized that the definitions of pH, the pH scale, and the values assigned to the Buffer Solutions for Standardization are for the purpose of establishing a practical, operational system so that results may be compared between laboratories. The pH values thus measured do not correspond exactly to those obtained by the classical definition, pH = $-\log [H^+(aq)]$. So long as the solution being measured is sufficiently similar in composition to the buffer used for standardization, the operational pH corresponds fairly closely to the theoretical pH. Although no claim is made with respect to the suitability of the system for measuring hydrogen-ion activity or concentration, the values obtained are closely related to the activity of the hydrogen ion in aqueous solutions.

Where a pH meter is standardized by use of an aqueous buffer and then used to measure the "pH" of a nonaqueous solution or suspension, the ionization constant of the acid or base, the dielectric constant of the medium, the liquid-junction potential (which may give rise to errors of approximately 1 pH unit), and the hydrogen-ion response of the glass electrode are all changed. For these reasons, the values so obtained with solutions that are only partially aqueous in character can be regarded only as apparent pH values. However, acidity may be accurately measured with the proper use of electrodes and instrument standardization.

Buffer Solutions for Standardization of the pH Meter-

Buffer Solutions for Standardization are to be prepared as directed in the accompanying table. Buffer salts of requisite purity can be obtained from the National Bureau of Standards. Solutions may be stored in chemically resistant, tight containers, such as Type I glass bottles. Fresh solutions should be prepared at intervals not to exceed 3 months. The table indicates the pH of the buffer solutions as a function of temperature. The instructions presented here are for the preparation of solutions having the designated molal (m) concentrations. For convenience, and to facilitate their preparation, however, instructions are given in terms of dilution to a 1000-mL volume rather than specifying the use of 1000 g of solvent, which is the basis of the molality system of solution concentration. The indicated quantities cannot be computed simply without additional information.

Potassium Tetraoxalate, 0.05 m—Dissolve 12.61 g of KH₃(C₂O₄)₂.2H₂O in water to make 1000 mL.

Potassium Biphthalate, 0.05 m-Dissolve 10.12 g of

¹ Commercially available buffer solutions for pH meter standardization, standardized by methods traceable to the National Bureau of Standards (NBS), labeled with a pH value accurate to 0.01 pH unit, and provided with a table showing the pH values at various temperatures, may be used. Solutions prepared from ACS reagent grade materials or other suitable materials, in the stated quantities, may be used provided the pH of the resultant solution is the same as that of the solution prepared from the NBS certified material.

| pH Values of Buffer Solutions | for Standardization |
|-------------------------------|---------------------|
|-------------------------------|---------------------|

| Temperature, °C | Potassium Tetraoxalate, 0.05 m | Potassium Biphthalate, 0.05 m | Equimolal Phosphate, 0.05 m | Sodium Tetraborate, 0.01 m | Calcium Hydroxide, Saturated at 25° |
|-----------------|--------------------------------------|-------------------------------------|-----------------------------|----------------------------------|---|
| 10 | 1.67 | 4.00 | 6.92 | 9.33 | 13.00 |
| 15 | 1.67 | 4.00 | 6.90 | 9.28 | 12.81 |
| 20 | 1.68 | 4.00 | 6.88 | 9.23 | 12.63 |
| 25 | 1.68 | 4.01 | 6.86 | 9.18 | 12.45 |
| 30 | 1.68 | 4.02 | 6.85 | 9.14 | 12.29 |
| 35 | 1.69 | 4.02 | 6.84 | 9.10 | 12.13 |
| 40 | 1.69 | 4.04 | 6.84 | 9.07 | 11.98 |
| 45 | 1.70 | 4.05 | 6.83 | 9.04 | 11.84 |
| 50 | 1.71 | 4.06 | 6.83 | 9.01 | 11.71 |
| 55 | 1.72 | 4.08 | 6.83 | 8.99 | 11.57 |
| 60 | 1.72 | 4.09 | 6.84 | 8.96 | 11.45 |

 $KHC_8H_4O_4$, previously dried at 110° for 1 hour, in water to make 1000 mL.

Equimolal Phosphate, 0.05 m—Dissolve 3.53 g of Na₂HPO₄ and 3.39 g of KH₂PO₄, each previously dried at 120° for 2 hours, in water to make 1000 mL.

Sodium Tetraborate, 0.01 m—Dissolve 3.80 g of Na₂B₄O₇.-10H₂O in water to make 1000 mL. Protect from absorption of carbon dioxide.

Calcium Hydroxide, saturated at 25°—Shake an excess of calcium hydroxide with water, and decant at 25° before use. Protect from absorption of carbon dioxide.

Because of variations in the nature and operation of the available pH meters, it is not practicable to give universally applicable directions for the potentiometric determinations of pH. The general principles to be followed in carrying out the instructions provided for each instrument by its manufacturer are set forth in the following paragraphs. Examine the electrodes and, if present, the salt bridge prior to use. If necessary, replenish the salt bridge solution, and observe other precautions indicated by the instrument or electrode manufacturer.

To standardize the pH meter, select two Buffer Solutions for Standardization whose difference in pH does not exceed 4 units and such that the expected pH of the material under test falls between them. Fill the cell with one of the Buffer Solutions for Standardization at the temperature at which the test material is to be measured. Set the "temperature" control at the temperature of the solution, and adjust the calibration control to make the observed pH value identical with that tabulated. Rinse the electrodes and cell with several portions of the second Buffer Solution for Standardization, then fill the cell with it, at the same temperature as the material to be measured. The pH of the second buffer solution is within ±0.07 pH unit of the tabulated value. If a larger deviation is noted, examine the electrodes and, if they are faulty, replace them. Adjust the "slope" or "temperature" control to make the observed pH value identical with that tabulated. Repeat the standardization until both Buffer Solutions for Standardization give observed pH values within 0.02 pH unit of the tabulated value without further adjustment of the controls. When the system is functioning satisfactorily, rinse the electrodes and cell several times with a few portions of the test material, fill the cell with the test material, and read the pH value. Use carbon dioxide-free water (see Water, in the section, Reagents, Indicators, and Solutions) for solution or dilution of test material in pH determinations.

Where approximate pH values suffice, indicators and test papers (see *Indicators and Indicator Test Papers*, in the section, *Reagents*, *Indicators*, and *Solutions*) may be suitable.

For a discussion of buffers, and for the composition of standard buffer solutions called for in compendial tests and assays, see Buffer Solutions, in the section, Reagents, Indicators, and Solutions.

(801) POLAROGRAPHY

Polarography is an electrochemical method of analysis based on the measurement of the current flow resulting from the electrolysis of a solution at a polarizable microelectrode, as a function of an applied voltage. The polarogram (see Figure 1) obtained by this measurement provides qualitative and quantitative information on electro-reducible and electro-oxidizable substances. The normal concentration range for substances being analyzed is from 10⁻² molar to 10⁻⁵ molar.

In direct current (dc) polarography, the microelectrode is a dropping mercury electrode (DME) consisting of small reproducible drops of mercury flowing from the orifice of a capillary tube connected to a mercury reservoir. A saturated calomel electrode (SCE) with a large surface area is the most commonly employed reference electrode. As the voltage applied to the cell increases, only a very small residual current flows until the substance under assay undergoes reduction or oxidation. Then the current increases, at first gradually, then almost linearly with voltage, and it gradually reaches a limiting value as is shown in Figure 1. On the initial rising portion of the polarographic wave, the increased flow of current results in a decrease in the concentration of the electro-active species at the electrode surface. As the voltage and current increase, the concentration of the reactive species decreases further to a minimal value at the electrode surface. The current is then limited by the rate at which the reacting species can diffuse from the bulk of the solution to the surface of the microelectrode. The final current rise is caused by the reaction of the supporting electrolyte. This large concentration of electrolyte is inert within the potential range used

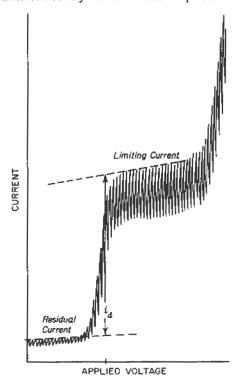


Fig. 1. Typical Polarogram Showing Change in Current Flow with Increasing Potential Applied to the Dropping Mercury Electrode.

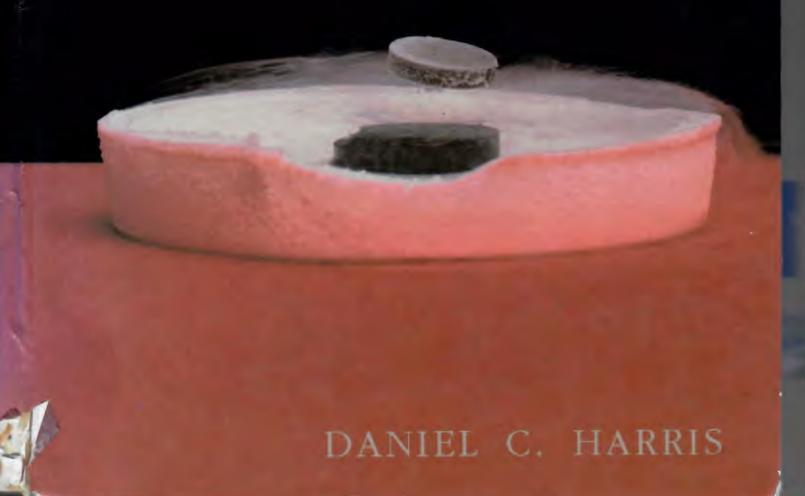
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EXHIBIT J

Case 1:20-cv-00110-JPB Document 198-1 Filed 11/21/23 Page 212 of 218 PageID #: 5189

THIRD EDITION

QUANTITATIVE CHEMICAL ANALYSIS



QUANTITATIVE CHEMICAL ANALYSIS

Third Edition

QUANTITATIVE CHEMICAL ANALYSIS

Third Edition

Daniel C. Harris

Michelson Laboratory
China Lake, California



W. H. Freeman and Company New York

Library of Congress Cataloging-in-Publication Data

Harris, Daniel C. 1948—
Quantitative chemical analysis / Daniel C. Harris. -3d ed.
p. cm.
Includes index.
ISBN 0-7167-2170-8 (hardcover) ISBN 0-7167-2171-6
1. Chemistry, Analytic Quantitative. I. Title.
QD101.2.H37 1991
545 dc20

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Printed in the United States of America

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90-38694 CIP

Figure 15-11
Ion-exchange equilibria on the inner and outer surfaces of the glass membrane.

365 15-5 pH MEASUREMENT WITH A GLASS ELECTRODE

The membrane is in equilibrium with H^+ on each surface, and Na^+ ions transport charge across the membrane so that one side still "senses" the other side. The mechanism of the glass electrode is therefore similar to that described for other ion-selective electrodes, except that the species that migrates across the membrane is not the same as the species selectively adsorbed at each membrane surface. The resistance of the glass membrane is typically $10^8 \ \Omega$, so very little current actually flows across it.

The potential difference between the inner and outer silver-silver chloride electrodes in Figure 15-8 depends on the chloride concentration in each electrode compartment and on the potential difference across the glass membrane. Since the chloride concentration is fixed in each electrode compartment, and since the H⁺ concentration is fixed on the inside of the glass membrane, the only factor causing a change in voltage is a change in pH of the analyte solution outside the glass membrane. The thermodynamic argument in the preceding section implies that for every factor-of-10 difference in H⁺ activity on each side of the membrane, a potential difference of 59.16 mV lat 25°C) should develop. That is, the voltage of the ideal pH electrode changes by 59.16 mV for every pH-unit change of the analyte.

For real glass electrodes, the response to changes in pH is nearly Nernstian and can be described by the equation

$$E = \text{constant } -\beta(0.059 \text{ 16}) \log \frac{\mathscr{A}_{\text{H}^+}(\text{inside})}{\mathscr{A}_{\text{H}^+}(\text{outside})}$$
 (at 25°C) (15-23)
Asymmetry
potential

Real electrodes come near to obeying the Nernst equation.

The pH electrode measures H⁺ activity, not H⁺ concentration.

The value of β , the electromotive efficiency, is close to 1.00 (typically > 0.98). It varies with each type of glass and with each individual electrode. The constant term, called the asymmetry potential, would be zero if both sides of the glass were identical. That is, no voltage would be observed if the activities of H⁺ were the same inside and outside and the membrane were ideal. However, no two sides of any real object are identical, and a small voltage exists even if \mathcal{A}_{H^+} is the same on both sides of the membrane. We correct for this asymmetry potential by calibrating the electrode in solutions of known pH. Because the asymmetry potential varies with time and conditions (temperature, concentrations, phase of the moon, color of your socks), electrodes must be calibrated frequently.

A pH electrode must be calibrated before it can be used, It should be calibrated about every two hours during sustained use.

Calibrating a Glass Electrode

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Many pH standards are available commercially. The pH values of the solutions in Table 15-3 were measured at the U.S. National Institute of Standards and Technology and are considered to be accurate to ± 0.01 pH unit.

Table 15-3
pH values of National Institute of Standards and Technology buffers

| Temperature (°C) | Saturated (25°C) potassium hydrogen tartrate | 0.05 m potassium dihydrogen citrate | 0.05 m potassium hydrogen phthalate | 0.025 m potassium dihydrogen phosphate 0.025 m disodium hydrogen phosphate | 0.008 695 m potassium dihydrogen phosphate 0.030 43 m disodium hydrogen phosphate | 0.01 m borax | 0.025 m sodium bicarbonate 0.025 m sodium carbonate |
|---------------------|---|--|--|---|--|-----------------|--|
| 0 | _ | 3.863 | 4.003 | 6.984 | 7.534 | 9,464 | 10.317 |
| 5 | _ | 3.840 | 3.999 | 6.951 | 7.500 | 9.395 | 10.245 |
| 10 | _ | 3.820 | 3.998 | 6.923 | 7.472 | 9.332 | 10.179 |
| 15 | _ | 3.802 | 3.999 | 6.900 | 7.448 | 9.276 | 10.118 |
| 20 | _ | 3.788 | 4.002 | 6.881 | 7.429 | 9.225 | 10.062 |
| 25 | 3.557 | 3.776 | 4.008 | 6.865 | 7.413 | 9.180 | 10.012 |
| 30 | 3.552 | 3.766 | 4.015 | 6.853 | 7.400 | 9.139 | 9.966 |
| 35 | 3.549 | 3.759 | 4.024 | 6.844 | 7.389 | 9.102 | 9.925 |
| 38 | 3.548 | | 4.030 | 6.840 | 7.384 | 9.081 | - |
| 40 | 3.547 | 3.753 | 4.035 | 6.838 | 7.380 | 9.068 | 9.889 |
| 45 | 3.547 | 3.750 | 4.047 | 6.834 | 7.373 | 9.038 | 9.856 |
| 50 | 3.549 | 3.749 | 4.060 | 6.833 | 7.367 | 9.011 | 9.828 |
| 55 | 3.554 | _ | 4.075 | 6.834 | _ | 8.985 | |
| 60 | 3.560 | _ | 4.091 | 6.836 | _ | 8.962 | _ |
| 70 | 3.580 | _ | 4.126 | 6.845 | - | 8.921 | |
| 80 | 3.609 | - | 4.164 | 6.859 | - | 8.885 | _ |
| 90 | 3.650 | _ | 4.205 | 6.877 | - | 8.850 | _ |
| 95 | 3.674 | _ | 4,227 | 6.886 | - There | 8.833 | _ |

Note: The designation m stands for molality.

In the buffer solution preparations, it is essential to use high-purity materials and to employ freshly distilled or deionized water of specific conductivity not greater than 5 micromho cm. Solutions having pH 6 or above ahould be stored in plastic containers, and preferably with an NaOH trap to prevent ingress of atmospheric carbon dioxide. They can normally be kept for 2-3 weeks, or slightly longer in a refrigerator.

- Saturated (25 C) potassium hydrogen tartrate, KHC₄H₄O₆. An excess of the salt is shaken with water, and it can be stored in this way. Before use, it should be filtered or decanted at a temperature between 22°C and 28 C.
- 2. 0.05 m potassium dihydrogen citrate, KH₂C₆H₅O₇. Dissolve 11.41 g of the salt in one liter of solution at 25 C.
- 0.05 m potassium hydrogen phthalate. Although this is not usually essential, the crystals may be dried at 110°C for an hour, then cooled in a desiccator. At 25 C, 10.12 g C₆H₄(CO₂H)(CO₂K) is dissolved in water, and the solution made up to one liter.
- 4. 0.025 m disodium hydrogen phosphate, 0.025 m potassium dihydrogen phosphate. The anhydrous salts are best used; each should be dried for two hours at 120°C and cooled in a desiccator, since they are slightly hygroscopic. Higher drying temperatures should be avoided to prevent formation of condensed phosphates. Dissolve 3.53 g Na₂HPO₄ and 3.39 g KH₂PO₄ in water to give one liter of solution at 25°C.
- 0.008 695 m potassium dihydrogen phosphate, 0.030 43 m disodium hydrogen phosphate. Prepare as in Step 4 and dissolve 1.179 g KH₂PO₄ and 4.30 g Na₂HPO₄ in water to give one liter of solution at 25°C.
- 6. 0.01 m sodium tetraborate decahydrate. Dissolve 3.80 g Na₂B₄O₄ · 10H₂O in water to give one liter of solution. This borax solution is particularly susceptible to pH change from carbon dioxide absorption, and it should be correspondingly protected.
- 7. 0.025 m sodium bicarbonate. 0.025 m sodium carbonate. Primary standard-grade Na₂CO₃ is dried at 250°C for 90 minutes and stored over CaCl₃ and Drierite. Reagent-grade NaHCO₃ is dried over molecular sieves and Drierite for two days at room temperature. Do not beat NaHCO₃, or it may decompose to Na₂CO₃. Dissolve 2.092 g of NaHCO₃ and 2.640 g of Na₂CO₃ in one liter of solution at 25°C.

SOURCE: R. G. Bates, J. Res. National Bureau of Standards, 66A, 179 (1962); and B. R. Staples and R. G. Bates, J. Res. National Bureau of Standards, 73A, 37 (1969). The instructions for preparing these solutions are taken, in part, from G. Muttock in C. N. Reilley, ed., Advances in Analytical Chemistry and Instrumentation (New York: Wiley, 1963), Vol. 2, p. 45. See also R. G. Bates, Determination of pH: Theory and Practice, 2nd ed. (New York: Wiley, 1973), Chap. 4.

The pH of the calibration standards should bracket the pH of the unknown.

Before using a pH electrode, you must calibrate it, using two (or more) standard buffers selected so that the pH of the unknown lies within the range of the pH values for the buffers. The exact calibration procedure is different for each model of pH meter, so consult the manufacturer's instructions for your meter. Before calibrating the electrode, wash it with distilled water and gently blot it dry with a tissue. Do not wipe it because this might produce a static electric charge on the glass.

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For calibration with most types of pH meters, dip the electrode in a standard buffer whose pH is near 7 and allow the electrode to equilibrate for at least a minute. For best results, all solutions for calibration and measurement should be stirred continuously during the measurement. Following the manufacturer's instructions, adjust the meter reading (usually with a knob labeled "Calibrate") to indicate the pH of the standard buffer. (If the meter has an adjustment of the "isopotential point," it should be set to the pH of this first buffer.) The electrode is then washed, blotted dry, and immersed in a second standard whose pH is further from 7 than the pH of the first standard. If the electrode response were perfectly Nernstian, the voltage would change by 0.059 16 V per pH unit at 25°C. The actual change is slightly less, so these two measurements serve to establish the value of β in Equation 15-23. The pH of the second buffer is set on the meter with a knob that may be labeled "Slope" or "Temperature" on different instruments. This effectively tells the meter the value of β . If your meter does not have an isopotential point adjustment, it may be necessary to repeat the calibration with the two buffers to obtain correct readings for each. Finally, the electrode is dipped in the unknown and the voltage is translated directly into a pH reading by the

A glass electrode must be stored in aqueous solution so that the hydrated gel layer of the glass does not dry out. If the electrode has been allowed to dry out, it should be reconditioned by soaking in water for several hours. If the electrode is to be used at a pH above 9, soak it in a high-pH buffer.

Glass electrodes slowly wear out, partly because the composition of the glass changes near the solution interface as ions diffuse in and out. If electrode response becomes sluggish or if the electrode cannot be calibrated properly, try washing it with 6 m HCl, followed by water. As a last resort, the electrode can be soaked in 20% (wt/wt) aqueous ammonium bifluoride, NH₄HF₂, for one minute in a plastic beaker. This reagent dissolves a little of the glass and exposes fresh surface. Wash the electrode with water and try calibrating it again. Ammonium bifluoride must not contact your skin, because it produces HF burns.

Errors in pH Measurement

To make intelligent use of a glass electrode, it is important to understand its limitations:

- Our knowledge of an analyte's pH cannot be any better than our knowledge of the pH of the buffers used to calibrate the meter and the electrode. This error is typically on the order of ±0.01 pH unit.
- 2. A junction potential exists across the porous plug near the bottom of the electrode in Figure 15-7. The porous plug is the salt bridge connecting the outer silver—silver chloride electrode with the analyte solution. If the ionic composition of the analyte solution is different from that of the standard buffer, the junction potential will change even if the pH of the two solutions is the same. This change appears as a change in pH and leads to an uncertainty in the pH of at least ~0.01 pH unit. Box 15-2 describes measurements in which junction potential changes lead to significant errors.
- 3. When the concentration of H⁺ is very low and the concentration of Na⁺ is high (a typical set of conditions in strongly basic solution), the electrode responds to Na⁺ as well as to H⁺. This arises because Na⁺ can participate in ion exchange with the hydrated gel layer.

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15-5 ph Measurement with a glass
Electrode

Do not leave a glass electrode out of water (or in a nonaqueous solvent) any longer than necessary.

The apparent pH will change if the ionic composition of the analyte changes, even when the actual pH is constant.